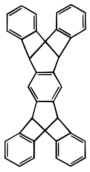
Porous Shape Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials

Jye-Shane Yang and Timothy M. Swager*

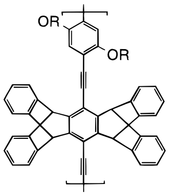
Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Ave., Cambridge, Massachusetts 02139

Received December 19, 1997

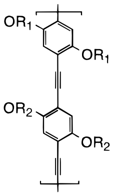
Fluorescence is a leading signal transduction method for the formation of chemosensory devices.[1,2] Conjugated polymer-based fluorescent chemosensors have been proven to further amplify this inherently sensitive method.[2] Although solid-state (thin film) fluorescent chemosensory devices are generally required, most systems have limited solid state utility with the lack of stable (reproducible) spectroscopic features and low fluorescence quantum yields, presumably due to the excimer formation and self-quenching.[3,4] These processes have been an impediment to other applications of conjugated polymers and general solutions also have implications for electroluminescent polymer devices.[4] We report herein an approach to stable fluorescent conjugated polymer films by the incorporation of the rigid three-dimensional pentiptycene moieties,[5] **1**, which prevent π-stacking or excimer formation. In comparison to the planar model polymer **3**, thin films of the pentiptycene polymer, **2**, display enhanced fluorescence quantum yield and stability. Moreover, their potential for the trace detection of high explosives such as 2,4,6-trinitrotoluene (**TNT**) is also reported.[6] Polymer **2** has unprecedented high sensitivity as an artificial fluorescent chemosensor for the vapors of **TNT** and 2,4-dinitrotoluene (**DNT**).



1



2



3

(R = $C_{14}H_{29}$; R_1 = C_8H_{17}; R_2 = $C_{16}H_{33}$)

The absorption and fluorescence spectra of the pentiptycene polymer, **2** (M_n = 56 000),[7] and **3** (M_n = 33 000),[8] in dichloromethane and thin films,[9] are shown in Figure 1. While **3** displays a substantial red shift (18−30 nm) in its principal absorption and fluorescence bands in thin films relative to solution, **2** shows almost invariant behavior in terms of the shape and positions ($\Delta\lambda_{max}$ = 4−7 nm) of its peaks. The persistence of a mirror-image relationship of **3**'s absorption and emission spectra with vibrational structure indicates that the red shift results from electronic perturbations due to π-stacking of polymer chains. The absence of similar perturbations for **2** in the solid state confirms that the rigid pentiptycene structure prevents significant π-stacking interactions between polymer backbones. Greatly reduced interpolymer interactions also account for the observed 100-fold larger solubility of **2** relative to **3** in organic solvents, despite **3** having more than double the density of side chains. In accord, the fluorescence quantum yield of **2** is 3.5 times larger than that of **3** in the thin films.[10]

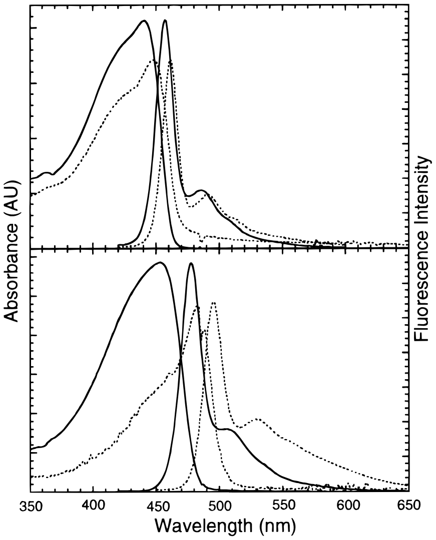


Figure 1. The absorption and fluorescence spectra of (A) **2** and (B) **3** in dichloromethane (full lines) and in spin-cast films (dot lines).

It appears that prevention of direct contact of conjugated backbones also contributes to the greater spectroscopic stability of polymer films of **2** relative to **3**. Fresh films of **2** exhibit small or no decrease (<10%) of fluorescence intensity with methanol washes or heating (140 °C) for 5 min, whereas the corresponding reduction of fluorescence in **3** is as large as 80%. Such changes are presumably due to solvent or heat-induced spatial re-organization of polymer packing (e.g. a change of adjacent polymer backbones from edge-on to face-on (π-stacking) structure). The influence of interpolymer reorganization on fluorescence behavior is expected to be small in cases where polymer backbones are not allowed to have direct contact.

Polymers **2** and **3** display fast fluorescence responses to **TNT** and **DNT**.[11] Figure 2 shows the time-dependent fluorescence intensity of **2** (25 ± 5 Å thickness)[12] upon exposure to **TNT** vapor. The fluorescence quenching increases to 50 ± 5% within 30 s

---

[1] *Chemosensors of Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic Publishers: Boston, 1997.

[2] (a) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. (b) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017.

[3] (a) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469. (b) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587. (c) Fox, M. A.; Fox, H. H. *Macromolecules* **1995**, *28*, 4570.

[4] (a) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765. (b) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

[5] (a) Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev.* **1974**, *43*, 951. (b) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641. (c) Shahlai, K.; Hart, H. *J. Org. Chem.* **1991**, *56*, 6905.

[6] Kolla, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 800.

[7] M_n was determined by GPC relative to polystyrene standards. Detailed synthetic procedures will be forthcoming.

[8] The synthesis of this polymer and its solution fluorescence has been reported previously: Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886.

[9] Polymer thin films were spin cast from chloroform solutions and placed under vacuum overnight before use.

[10] (a) Due to the lack of reliable references, absolute fluorescence quantum yields of polymer films were not determined. The fluorescence quantum yields of **2** and **3** in dilute CH_2Cl_2 solution are 0.50 and 0.27, respectively, with anthracene in hexane (quantum yield = 0.27)[10b] as the actinometer. The corresponding lifetime data (0.51 and 0.54 ns, respectively)[10c] suggest that the rate constants of fluorescence reach the maximum (10^9 s^{-1}) for organic molecules in the case of **2**. Assuming similar rate constants in the thin films, the 6-fold shorter lifetime of **2** in a thin film (ca. 87 ps) than in solution suggests a 6-fold decrease of fluorescence yield from a dilute solution to a solid-state film. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970. (c) Fluorescence lifetimes were determined by the phase-modulation technique with a SPEX Fluorolog instrument.

[11] Analytes (quenchers) were placed in small sealed vials containing cotton gauze, which provides a high surface area to maintain a constant vapor pressure. The polymer thin films were inserted in the vial for a specific time and then subjected to immediate fluorescence measurements. The excitation wavelengths for **2** and **3** are 400 and 430 nm, respectively.

[12] The film thickness was determined by ellipsometry. An excellent linear relationship of optical density and ellipsometric data was established and this allows the film thickness to be measured in cases that the polymer film is too thin to be measured accurately by ellipsometry.

S0002-7863(97)04299-6 CCC: $15.00

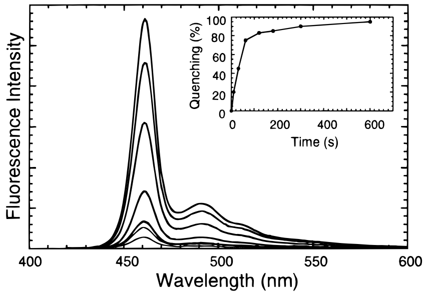


Figure 2. The time-dependent fluorescence intensity of **2** (25 ± 5 Å thickness) upon exposure to **TNT** vapor (room temperature) at 0, 10, 30, 60, 120, 180, 300, and 600 s (top to bottom) and the fluorescence quenching (%) against time (inset).

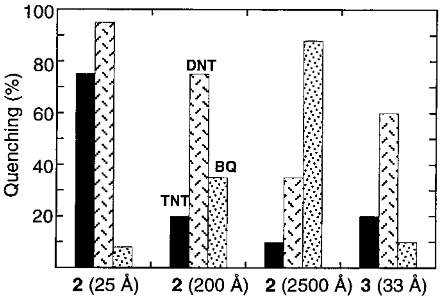
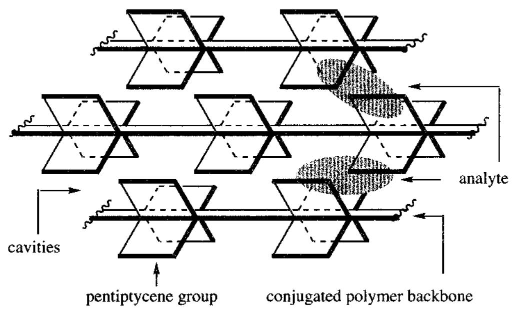


Figure 3. The amount of fluorescence quenched by **TNT**, **DNT**, and **BQ** (room temperature) at an exposure time of 60 s in films **2** and **3**.

and to 75 ± 5% at 60 s (Figure 2, inset). The response of the same film to **DNT** vapor is even faster (e.g. 91 ± 2% fluorescence quenching at 30 s), and can be attributed to the higher equilibrium vapor pressure[13] of **DNT** (1.47×10^{-4} mmHg at 22 °C) relative to **TNT** (8.02×10^{-6} mmHg at 25 °C). The fluorescence quenching is dependent on film thickness (Figure 3). For example, in a 25 Å film of **2** the amount of **DNT** quenching at 60 s is 95 ± 2%; however, this is reduced to 75 ± 5% in a 200-Å film and is only 35 ± 5% in a 2500-Å film. Ironically, with benzoquinone (**BQ**) vapor (0.9 mmHg at 20 °C), a faster response was found for thicker films of **2**. Due to lower solubility of **3**, we were limited to $\sim$33 Å films. In response to **TNT**, **DNT**, and **BQ**, we observed a relatively slower response for **3** vs **2** with similar film thickness (Figure 3). Thin films of both **2** and **3** have slow response to **BQ**; however, prolonged exposure to **BQ** increases the fluorescence quenching for **2** (e.g. 8% at 1 min and 40% at 10 min) but not for **3** (e.g. 10% at both 1 and 10 min). A survey of several representative small aromatic compounds,[14] including 1,4-dimethoxybenzene, 1,4-dichlorobenzene, 1,4-dicyanobenzene, benzophenone, and 3,3′-dinitrobenzophenone, reveals that the size and electronic properties of the analyte are critical to obtain a response. In general, these species result in little or no fluorescence quenching (<10%) with exposure times of 5 min. Another important consideration is the fluorescent reversibility of the polymer films. Most of the initial fluorescence of thin films of **2** after exposure to quenchers can be recovered (70−100%) by rinsing with methanol and gentle air drying; however, the fluorescent reversibility of **3** is poor (<30%), probably due to its poor solvent stability.

The mechanism of fluorescence attenuation can be attributed to the electron transfer from the excited polymer to the electron acceptors (**TNT**, **DNT**, and **BQ**).[15] Although **BQ** has the highest vapor pressure and is most readily reduced, it shows the least amount of fluorescence quenching in **3** and in 25-Å films of **2**. This may result from weaker $\pi-\pi$ interactions between the π-electron rich polymers and **BQ** molecules due to differences in its charge distribution relative to **TNT** or **DNT**.[16] The large response to **BQ** in thicker films is consistent with films of **2** having a porous nature due to the three-dimensional pentiptycene scaffold.[17] The greater number of cavities in thicker films would more effectively sequester **BQ**, which has higher volatility. Scheme 1 shows a conceptual and idealized model of the structure obtained in thin films of **2**. It should be noted that the polymer backbones are not expected to have a perfectly parallel alignment. The porous nature of **2**'s films is likely the origin of its larger response to **BQ** in comparison to **3**. **TNT** and **DNT**, on the other hand, due to their stronger interactions with the polymers, lower volatility, and larger size, may favor binding near the film's surface. Consequently, the interior of thicker films is not readily quenched due to the limited distance of energy migration, which is a result of the short excited-state lifetime of the polymers in the film.[10,18] Nevertheless, films of **3** show considerably less quenching by **TNT** and **DNT** than films of **2** with similar thickness ($\sim$30 Å). Further studies on the electronic and structural influence of these systems are in progress in order to gain an insight into the binding character.

Scheme 1



In summary, the pentiptycene-derived conjugated polymer, **2**, is an excellent fluorescent chemosensor for the detection of electron-deficient unsaturated species including **TNT**, **DNT**, and **BQ**. The manipulation of the thickness of polymer films allows differentiation of **BQ** from the other quenchers. The rigid pentiptycene scaffold also provides a new method to improve the luminescent properties of films for sensor and electroluminescent applications. Moreover, these materials are less prone than other conjugated polymers to emission changes resulting from structural reorganization. More elaborated rigid scaffolds attached to conjugated polymers should supply the necessary selectivity to form reliable sensors.

Acknowledgment. The authors acknowledge financial support from The Office of Naval Research and The Defense Advanced Research Projects Agency for funding. Additional appreciation is due to Professor M. G. Bawendi for the use of his spin coater, Mr. Sean McHugh, who generously supplied polymer **3**, Mr. Jinsang Kim for the help of determining film thickness, and to Dr. Vance Williams for helpful discussions.

JA9742996

---

[13] Equilibrium vapor pressures are obtained from the following: *Handbook of Physical Properties of Organic Chemicals*; Howard, P. H., Meylan, W. M., Eds.; CRC Press: Boca Raton, FL, 1997.

[14] All exhibit a vapor pressure higher than that of **DNT**.[13]

[15] The reduction potentials of **BQ**, **TNT**, and **DNT** are ca. -0.5, -0.7, and -1.0 V vs SCE in acetonitrile. *Handbook Series in Organic Electrochemistry* Meites, L., et al., Eds. CRC Press: Boca Raton, FL, 1978, Vol 1.

[16] (a) The relative electrostatic potential in the center of the ring on the van der Waals surface was calculated[16b] to be 34.62, 19.21, and 13.85 kcal/mol for **TNT**, **DNT,** and **BQ**, respectively. (b) Calculations were performed by AM1 in MACSPARTAN, a product of Wavefunctions, Inc., CA. (c) For recent discussions of aromatic electrostatic interactions see: Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019. Williams, V. E.; Lemieux, R. P.; Thatcher, G. R. J. *J. Org. Chem.* **1996**, *61*, 1927.

[17] Iptycenes tend to form cavities in the solid state. For examples see: (a) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675. (b) Venugopalan, P.; Bürgi, H.-B.; Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 2419.

[18] Energy migration is present in the polymer thin films as evidenced by fluorescence polarization measurements before and after exposure to **TNT** for 5 min (anisotropy = 0.01 and 0.35, respectively). The lack of polarization in the initial films indicates that extensive energy migration occurs in thin films, whereas the latter indicates that greater spatial diffusion of the excitations, which would ordinarily lead to greater depolarization, increases the probability of quenching by **TNT**.