ChemComm
RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Extremely fast and highly selective detection of nitroaromatic explosive vapours using fluorescent polymer thin films†

Gokcen Birlik Demirel,*[ab] Bihter Daglar[ac] and Mehmet Bayindir*[acd]

Cite this: *Chem. Commun.*, 2013, **49**, 6140

Received 30th April 2013,
Accepted 21st May 2013

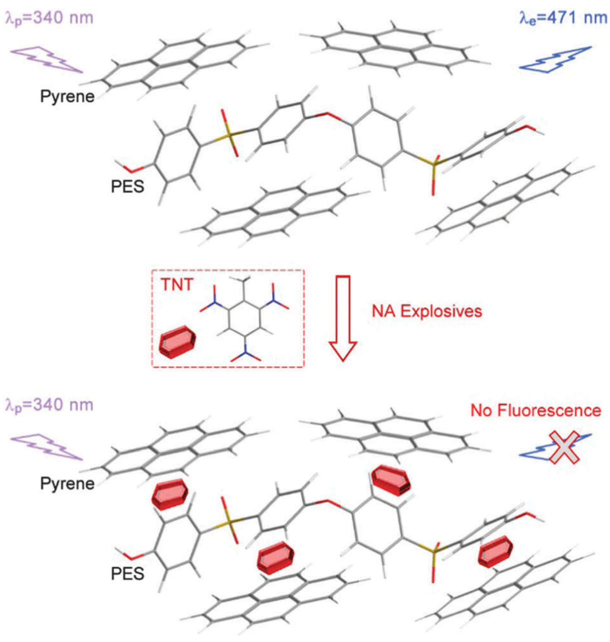
DOI: 10.1039/c3cc43202e

www.rsc.org/chemcomm

A novel sensing material based on pyrene doped polyethersulfone worm-like structured thin film is developed using a facile technique for detection of nitroaromatic explosive vapours. The formation of π–π stacking in the thin fluorescent film allows a highly sensitive fluorescence quenching which is detectable by the naked eye in a response time of a few seconds.

Nitroaromatic (NA) explosives are the primary constituents of many unexploded land mines worldwide.[1,2] Selective, fast and low-cost detection of NA explosives, such as trinitrotoluene (TNT) and dinitrotoluene (DNT), is crucial for military operations, homeland security, and environmental safety.[3] Various analytical and spectroscopic methods have been developed for sensitive detection of NA compounds.[4–7] These instrumental techniques are mostly expensive and not portable for use in the field. The detection of NA explosives using fluorescent-based sensors has been extensively studied because of their sensitivity, portability, and short response time.[8–13] The most important report in this field was published by Swager' group.[14] They used a conjugated polymer scaffold and improved the detection sensitivity.[14] Trogler and co-workers developed a new class of fluorescent films which were fabricated by spin-coating onto suitable solid substrates for detecting NA explosives both in the air and organic solvents.[15] The underlying explosive detection mechanism of the fluorescent polymer is photo-induced electron transfer (PET) from the polymers to the NA explosives. The key feature of this phenomenon is the presence of the π–π-stacking (excimer) between the polymer chains and chromophore groups. This π-stacked formation can significantly enhance the sensing performance of films.[14,15]

In this report, we have fabricated a novel fluorescent thin film based on the pyrene-doped polyethersulfone (Py-PES) polymer for detection of nitro-explosive vapours using a rapid and facile method. The experimental details of the preparation of this sensing film are given in ESI.† To prepare the fluorescent polymer, we chose pyrene (Py) as the fluorescent dye because of its potential to form highly emissive excited dimers, high fluorescence yield, and known fluorescence quenching sensitivity to NA compounds.[16] The driving force for the quenching mechanism of Py-PES thin films is the formation of π–π



Scheme 1 Schematic representation of the quenching mechanism for the Py-PES film by TNT based on photo-electron transfer (PET) process. The main driving force for the PET process is the energy gap between the conduction band of Py-PES films and the LUMO of NA explosives. NA explosives accept the electron from exited state of pyrene due to their low LUMO energies and as a result the fluorescent film is quenched[18] (see details in ESI†).

---

[a] *UNAM-National Nanotechnology Research Center, Bilkent University, 06800 Ankara, Turkey. E-mail: birlik@unam.bilkent.edu.tr*
[b] *Department of Chemistry, Gazi University, Polatli, 06900, Ankara, Turkey*
[c] *Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey*
[d] *Department of Physics, Bilkent University, 06800 Ankara, Turkey. E-mail: bayindir@nano.org.tr*

† Electronic supplementary information (ESI) available: Experimental details, DFT calculation of HOMO and LUMO band energies of PES, AFM image of Py-PES thin films, and fluorescent emission spectra of Py-PES thin films. See DOI: 10.1039/c3cc43202e

stacking between pyrene and the PES monomer in the thin film. The formation of a sandwich-like (Scheme 1) conformation of the Py-PES film made it possible for pyrene monomer or excimer units to be inserted into and between the phenyl groups of PES and thus led to the formation of extended conjugation of π electrons.[17] To reveal the PET mechanism between Py-PES thin films and NA explosives, we calculated HOMO and LUMO energies of PES films using DFT calculation. The calculation details and HOMO and LUMO energies of PES, pyrene and NA explosives are given in ESI.†

As mentioned before, the π-conjugation in the polymer film is an effective way to enhance the sensing performance.[15] We characterized the formation of π–π stacking between the PES polymer and pyrene molecules in the sensing film with high resolution C1s XPS spectra (Fig. 1a). We observed the π–π stacking of C atoms at 288.9 eV.[19,20] Moreover, the characteristic C–O and C–C binding energy peaks of the Py-PES polymer also appeared at 286.0 eV and 284.5 eV, respectively.[19]

The Py-PES solution was prepared in THF and then spin coated on the glass surface (see the experimental details in ESI†). To reveal the structural formation of coated Py-PES films, SEM images shown in Fig. 1b were taken. As seen in the images, the Py-PES film formed a 'worm-like' structure on the glass substrate.

The sensing performance of the Py-PES thin film was tested with incubation of TNT vapour. Fig. 2a shows the time-dependent fluorescence spectra of the Py-PES film upon exposure to equilibrium TNT vapour. The Py-PES film exhibited extremely fast sensing response against TNT vapour. The fluorescence quenching of excimer emissions was observed to be nearly 50% at 471 nm within 15 s and more than 95% was achieved within 60 s (Fig. 2b).

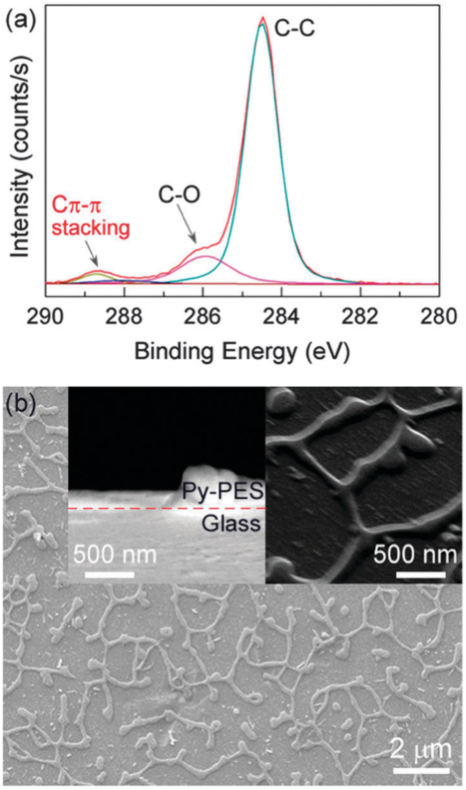


Fig. 1 (a) The C1s XPS spectra; (b) SEM image of the Py-PES thin film (top left inserted image; cross-section and top right inserted image; 30° tilted version of the same surface).

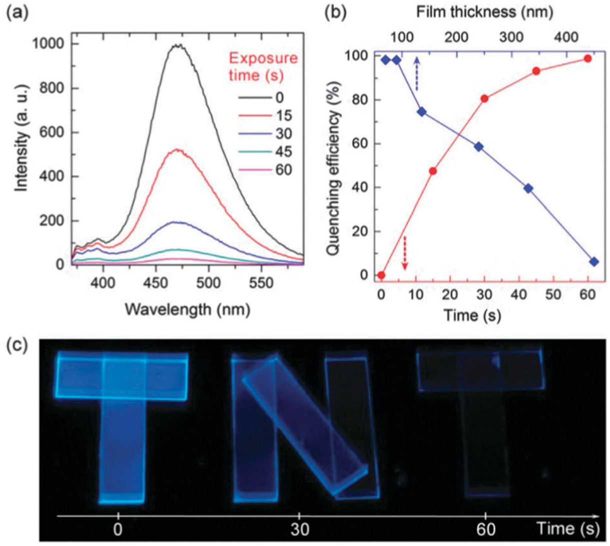


Fig. 2 (a) The time-dependent fluorescence intensity of Py-PES thin film upon exposure to equilibrium TNT vapours; (b) the quenching efficiency of Py-PES films with changing time and film thickness (red line indicates the quenching efficiency of 90 nm PES film); (c) photograph of Py-PES thin films under 366 nm UV light before (t = 0) and after exposure to TNT for 30 s and 60 s, respectively.

To evaluate the effect of film thickness on the quenching efficiency of the Py-PES film, we prepared various films as described in ESI.† As seen in Fig. 2b, more than 95% quenching was observed for 90 nm and 70 nm thin films while 75%, 59%, and 40% quenchings were observed for 136 nm, 240, and 330 nm thick films, respectively. Parallel to our results, we found that the 450 nm thick Py-PES film exhibited the lowest quenching efficiency due to the low diffusion of TNT molecules into the thicker films and the limited distance of energy migration.[3] It is obvious that the fluorescence quenching is inversely correlated with the film thickness. The results showed that to obtain the highest quenching efficiency, the thickness of the Py-PES film should be below 100 nm and thereby we have utilized 90 nm Py-PES thin films in the rest of the work. Both electronic features and the porosity of the resultant polymer films are crucial for determining the fluorescence sensitivity of NA explosives.[3] The 'worm-like' structured Py-PES polymer thin film has a rough surface that may increase the diffusion of TNT throughout the film. Therefore we believe that 'worm-like' structure of the Py-PES thin film may be responsible for enhancement of the quenching efficiency.

According to these results it can be clearly said that this new sensing material is very facile, rapid, robust and cost effective compared to conjugated polymers reported in the literature.[21–23]

In addition, the NA explosive vapours can be simply detected by the naked eye under a simple UV lamp in less than 1 min without the need for any expensive instrument (Fig. 2c). As a result, we can clearly say that this sensing film has potential to be used as a portable NA explosive sensor in the application areas.

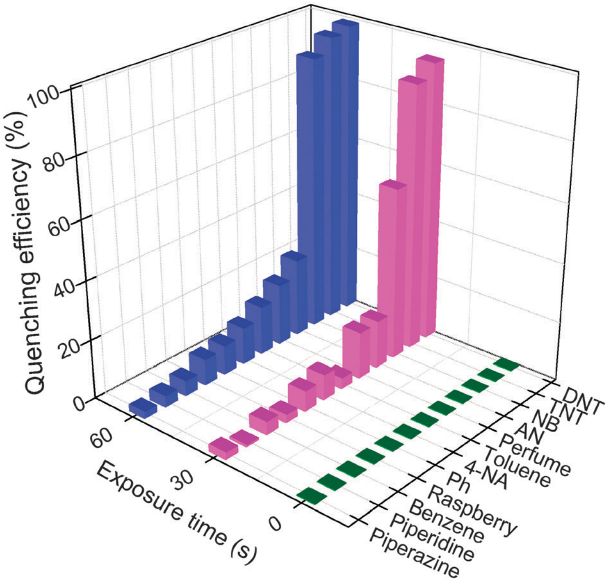


Fig. 3 The time-dependent fluorescence quenching efficiencies at 471 nm for saturated vapours of different chemicals on Py-PES thin films.

Selectivity plays a crucial role in the functional application of a sensing film. Thereby we examined the quenching response of the Py-PES film to different chemicals that may affect the detection efficiency of NA explosive vapours (Fig. 3). The results showed that the Py-PES films exhibit selective quenching responses for different compounds. The pyrene excimer band (at 471 nm) is quenched by 95% for DNT vapour within 30 s, while this value decreases to 90% and 58% for TNT and NB, respectively (Fig. 3). It can be said that the Py-PES film is much more sensitive to DNT vapour than to TNT and other NA explosive vapours. It is known that the saturated vapour pressures of DNT and TNT are 1.1×10^{-4} mmHg (1.47×10^2 ppb) and 5.8×10^{-6} mmHg (7.7 ppb) at 25 °C, respectively.[13,24,25] This difference of the saturated vapour pressures of DNT and TNT may affect the sensing performance of the Py-PES films.[14,15] We observed the quenching performance of films following the order of DNT > TNT > NB. We also tested the selectivity of films to the vapours of some aromatic organic compounds, nonaromatic toxic compounds, perfume, and coffee syrup (raspberry). We observed no significant change in quenching response of the films upon exposure to these analytes. As mentioned above the selectivity of the Py-PES film was also investigated with nonaromatic toxic compounds; piperidine and piperazine. The Py-PES thin film exhibited no remarkable quenching response to nonaromatic toxic compounds due to the absence of strong π–π stacking between Py-PES and nonaromatic compounds. The results showed that Py-PES films display high selectivity towards NA compounds.

The Py-PES film showed different quenching performance to TNT, DNT and NB explosive vapours. This effect can be explained as a result of the differences between vapour pressures of NA explosives on the film surface. Hence the sensitivity of the Py-PES film towards the different chemicals may be understood by considering this factor.[14,26]

We have developed a novel sensing material based on a pyrene doped PES thin film for the fluorescence detection of NA explosive vapours. This fluorescent thin film can be used for extremely fast, selective and portable detection of trace amounts of NA explosive vapours. The sensing performance of the Py-PES film could be a reason for strong π–π stacking between pyrene molecules and phenyl rings of the PES polymer. The pyrene-doped PES polymer formed 'worm-like' structure on the surface. This 3D and porous structure of the thin polymer film may have caused the enhancement of quenching efficiency due to the easy diffusion of NA explosives throughout the film. Therefore, the Py-PES thin film exhibits promising potential as an easy, portable, cheap, sensitive and extremely fast-response sensor material for detection of NA explosives. It is safe to conclude that the Py-PES thin film should be a strong candidate for explosive sensory materials.

The authors are thankful to AdemYildirim, Pinar Beyazkilic and Fahri Emre Ozturk for fruitful discussion. This work was partially supported by TUBITAK under the Project No. 110M412 and 111T696. M.B. acknowledges partial support from the Turkish Academy of Sciences (TUBA).

Notes and references

1 T. F. Jenkins, D. C. Leggett, P. H. Miyares, M. E. Walsh, T. A. Ranney, J. H. Cragin and V. George, *Talanta*, 2001, **54**, 501.
2 J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864.
3 J. Yinon, *Anal. Chem.*, 2003, **75**, 99A.
4 (*a*) R. Hodyss and J. L. Beauchamp, *Anal. Chem.*, 2005, **77**, 3607; (*b*) I. A. Popov, H. Chen, O. N. Kharybin, E. N. Nikolaev and R. G. Cooks, *Chem. Commun.*, 2005, 1953.
5 L. Yang, L. Ma, G. Chen, J. Liu and Z.-Q. Tian, *Chem.–Eur. J.*, 2010, **16**, 12683.
6 E. L. Holthoff, D. N. Stratis-Cullum and M. E. Hankus, *Sensors*, 2011, **11**, 2700.
7 M. Berg, J. Bolotin and T. B. Hofstetter, *Anal. Chem.*, 2007, **79**, 2386.
8 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537.
9 M. R. Huang, S. J. Huang and X. G. Li, *J. Phys. Chem. C*, 2011, **115**, 5301.
10 M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543.
11 Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chem. Soc. Rev.*, 2012, **41**, 1261.
12 A. Yildirim, H. Acar, T. S. Erkal, M. Bayindir and M. O. Guler, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4159.
13 A. Yildirim, H. Budunoglu, H. Deniz, M. O. Guler and M. Bayindir, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2892.
14 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
15 J. C. Sanchez, S. A. Urbas, S. J. Toal, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Macromolecules*, 2008, **41**, 1237.
16 Y. H. Lee, H. Liu, J. Y. Lee, S. H. Kim, S. K. Kim, J. L. Sessler, Y. Kim and J. S. Kim, *Chem.–Eur. J.*, 2010, **16**, 5895.
17 K. S. Focsaneanu and J. C. Scaiano, *Photochem. Photobiol. Sci.*, 2005, **4**, 817.
18 Y. Wang, A. La, C. Bruckner and Y. Lei, *Chem. Commun.*, 2012, **48**, 9903.
19 Y. Setsuhara, K. Cho, K. Takenaka, M. Shiratani, M. Sekine and M. Horic, *Thin Solid Films*, 2011, **519**, 6721.
20 Y. Liu, Z. Du, Y. Li, C. Zhang, X. Yang and H. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6880.
21 Y. Long, H. Chen, H. Wang, Z. Peng, Y. Yang, G. Zhang, N. Li, F. Liu and J. Pei, *Anal. Chim. Acta*, 2012, **744**, 82.
22 H. Nie, G. Sun, M. Zhang, M. Baumgarten and K. Müllen, *J. Mater. Chem.*, 2012, **22**, 2129.
23 S. Zahn and T. M. Swager, *Angew. Chem., Int. Ed.*, 2002, **41**, 4225.
24 P. H. Howard and W. M. Meylan, *Handbook of Physical Properties of Organic Chemicals*, CRC-Press, Boca Raton, 1997.
25 J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Chem. Mater.*, 2007, **19**, 6459.
26 G. He, G. Zhang, F. Lü and Y. Fang, *Chem. Mater.*, 2009, **21**, 1494.