Supplementary Information

Extremely fast and highly selective detection of nitroaromatic explosive vapours by fluorescent polymer thin film

Gökçen Birlik Demirel,*[ab] Bihter Dağlar[ac] and Mehmet Bayındır*[acd]

[a]*UNAM-National Nanotechnology Research Center, Bilkent University 06800 Ankara, Turkey*
E-mail: birlik@unam.bilkent.edu.tr
[b]*Department of Chemistry, Gazi University, 06500 Besevler, 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

Materials

Polyethersulfone (PES) was purchased from Ajedium, USA. Tetrahidrofuran (THF), pyrene (Py), aniline (AN), nitrobenzene (NB), 4-nitroaniline (4-NA), toluene, phenol, piperazine, and piperidine were purchased from Sigma-Aldrich. All reagents were used as received without further purification. Coffee syrup (raspberry) and perfume were obtained from a local market.

Preparation of Py-PES Films

Pyrene-doped PES (Py-PES) films were all prepared using the same solution for spin coating which contains PES (2 mg/mL) and pyrene (0.1M) in THF. Spin-coating film was developed by spinning (Laurell Technologies WS650SZ-6NPP-lite spin coater) solution (100 µL) on glass slides (2.5 cm × 2.5 cm) with a spin rate of 4000 rpm. The ellipsometric thickness of the produced film was measured as 90 nm.

We also investigated the effect of film thickness on the quenching efficiency of the films. To this end we coated Py-PES (2 mg/mL) polymer on the glass surface with different spin rates. We produced 70 nm, 90 nm, and 136 nm Py-PES (2mg/mL) films using 5000 rpm, 4000 rpm, and 2500 rpm spin rates, respectively. In addition, 330 nm and 450 nm thick films were coated (2000 rpm) on the glass surface by using 3 mg/mL and 4 mg/mL polymer solutions, respectively.

Fluorescence Quenching Experiment

The fluorescence quenching experiments were performed similar to the previous reports.[1,2] Briefly a small amount of TNT or DNT powder were placed into a 10 mL vial and covered with cotton to prevent direct contact of the analyte molecules with the films and equilibrated for 48 h to ensure saturation reached. The glass slide, which is coated with Py-PES sensing film, was inserted into the vial at the 45 degree angle. After the film was placed in the cell, and the emission spectrum was collected every 30 s in the wavelength region of 360–600 nm with an excitation wavelength of 340 nm. The quenching experiments towards equilibrium vapours of other NA compouns (NB and 4-NA) and controls (AN, Benzene, Toluene, Phenol, Piperidine, Piperazine, Perfume, and Raspberry syrup) were conducted in a similar way.

To visualize the detection of NA explosives by naked eye, prepared Py-PES film was treated with a trace amount of TNT vapor for 60 seconds. A handheld UV lamp (λ_{ex} 366 nm) is used to reveal the quenching of film and to visualize by naked eye after 60 second exposure time. The photograph was taken to show the quenching of the whole film.

Characterization of Py-PES Films

Fluorescence emission spectrum was measured by a Varian Cary Eclipse fluorescence spectrophotometer. The chemical characterization of sensing film was performed using Thermo K-Alpha-Monochromated high-performance XPS spectrometer. SEM images of Py-PES films were performed by FEI Quanta 200 FEG Environmental Scanning Electron Microscope. The surface topology images and surface roughness of sensing film were collected by PSIA Atomic force microscopy (XE-100E) in tapping mode. The surface thicknesses of fluorescent films were measured with V-VASE Ellipsometer (J. A.Woollam). Here, the ellipsometric measurements of the layers were made on glass substrate by assuming the refractive index of layers as 1.5.

Calculation of HOMO and LUMO Energies of PES

The calculation of HOMO-LUMO energies for optimized geometry of PES are performed using the Vienna ab-initio simulation package (VASP)[3,4] which is a DFT code, operating in a plane-wave basis set. The electron interaction was considered in the form of the pseudopotantial with plane-waves up to an energy of Ecut = 25 Ry. This cut-off was found to be adequate for the structural studies as well as for the electronic structure. For exchange and correlation terms, the functional proposed by Perdew and Zunger[5] is used with (non-local) generalized gradient corrections (GGA)[6].

We determined the HOMO-LUMO energies of PES ($n=\infty$) using linear extrapolation of the property of geometry-optimized corresponding oligomers ($n=1$, $n=2$ and $n=4$). The each energy was plotted against the inverse of the total number of monomer unit ($1/n$) on the PES backbone. Then the lines were intercepted at origin (infinite number of monomers) represents the property of a polymer with a degree of polymerization of infinity[7,8]. Figure S1 represents the relationship between HOMO-LUMO energies and the reciprocal of monomers in PES chains. The HOMO and LUMO energies of PES were determined as -4.68 and -1.81 eV, respectively.

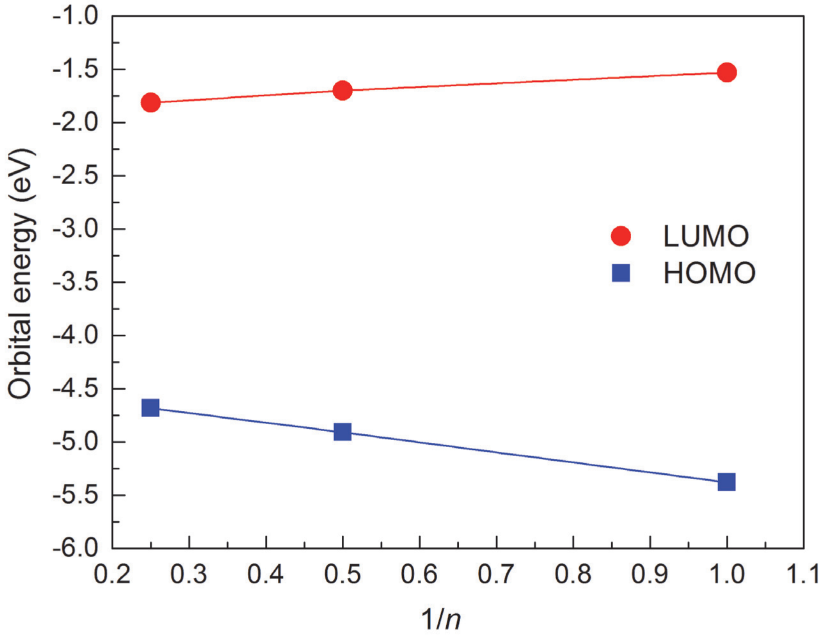


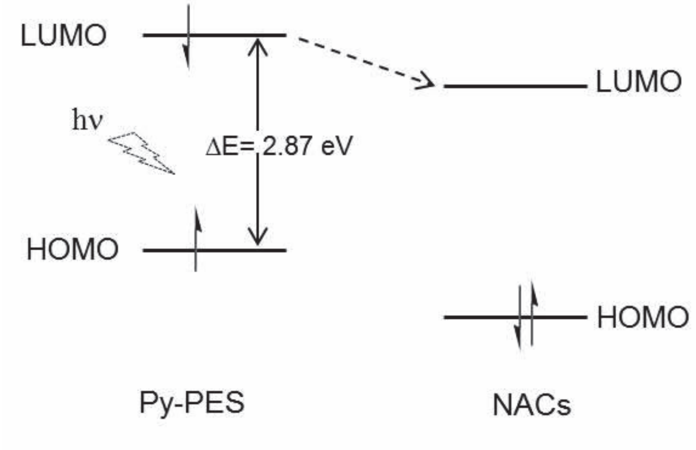
Fig. S1 Plots of the HOMO and LUMO energies of PES as a function of the repeat monomer units.

The HOMO-LUMO energies of NA explosives, and pyrene were adopted from literature which were calculated at the B3LYP/6-31G* level of theory and were given in Table S1.

Table S1 The calculated HOMO and LUMO energies of PES, pyrene and some NA explosives.

	HOMO (eV)	LUMO (eV)
PES	-4.68	-1.81
Pyrene[7]	-5.33	-1.48
TNT[7]	-8.46	-3.49
DNT[7]	-8.11	-2.98
NB[7]	-7.36	-2.31

The calculated band energies of PES are in accordance with the band energies of pyrene and NA compounds for photoinduced electron transfer (PET). Therefore the quenching process of Py-PES thin films could be assumed as PET. Here the main driving force for PET process is the energy gap between the conduction band of Py-PES film and the LUMO energy 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 as seen Scheme S1.



Scheme S1 Photoinduced electron transfer mechanism for Py-PES films by nitro explosive.

Fluorescent Emission Spectrum of Py-PES Films

As known that, the doping amount of fluorescent dye into the polymer composition plays an important role for the formation of π–π stacking between polymer and chromophore groups. The fluorescence emission of pyrene doped PES film, with and without π-π stacking, was given in Figure S2. As mentioned above, in the formation of π–π stacking between phenyl-rings of PES polymer and pyrene molecules, the intense emission band of excimer was observed at 471 nm besides the emission bands of monomeric pyrene in the near UV region (at 376 and 396 nm).[9] The presence of excimer emissions from the Py-PES conjugate shows that the loading of pyrene is high enough that π-stacked dimers have formed. On the other hand, in the emission spectrum of Py-PES film without π–π stacking (red line); only the emission bands of monomeric pyrene were observed in the near UV region not to have enough pyrene into the Py-PES composition.

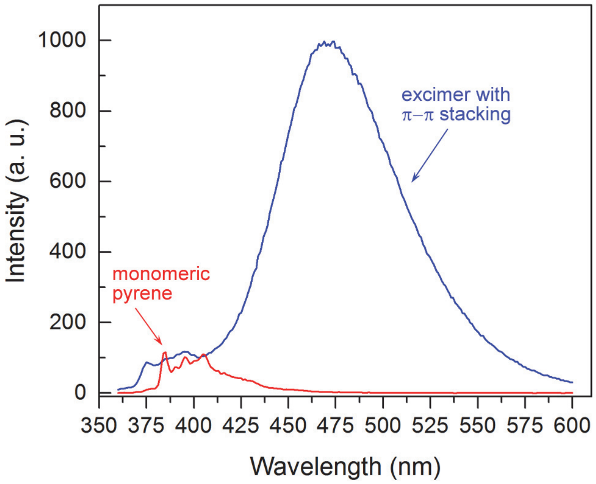


Fig. S2 The emission spectrum of Py-PES thin film with and without π–π stacking formation.

Surface Topography of Py-PES Thin Film

As seen in 3D-AFM image of the prepared fluorescent thin film, the pyrene-doped PES film formed 'worm-like' structure on the glass substrate. We measured the surface roughness of the film as 50 nm.

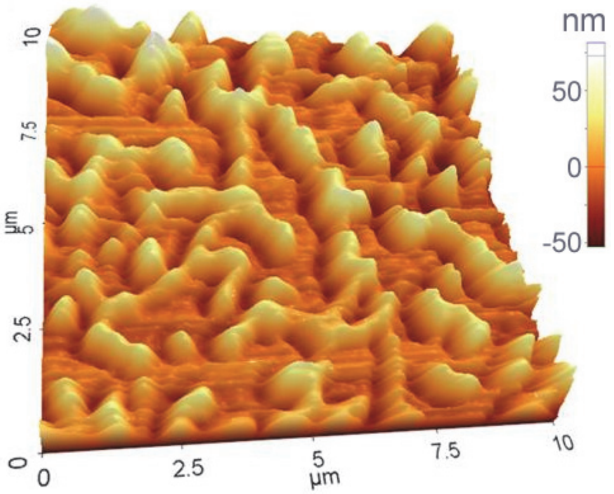


Fig. S3. 3D-AFM image of Py-PES worm-like structured thin film. The AFM image was collected in tapping mode for 10x10 µm area.

---

[1] A.Yildirim, H. Budunoglu, H. Deniz, M. O. Guler, M. Bayindir, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2892.

[2] Y. Wang, A. La, Y. Ding, Y. Liu, Y. Lei, *Adv. Funct. Mater.*, 2012, **22**, 3547.

[3] G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.

[4] G. Kresse, D. Joubert, *Phys. Rev. B, 1999,* **59,** 1758.

[5] J. P. Perdew, A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048

[6] J. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.

[7] Y. C. Hung, J. C. Jiang, C. Y. Chao, W. F. Su, S. T. Lin, *J. Phys. Chem. B.* 2009, **113**, 8268.

[8] G. He, N. Yan, J. Yang, H. Wang, L. Ding, S. Yin, Y. Fang, *Macromolecules,* 2011, **44,** 4759.

[9] K. S. Focsaneanu, J. C. Scaiano, *Photochem. Photobiol. Sci.*, 2005, **4**, 817.