

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

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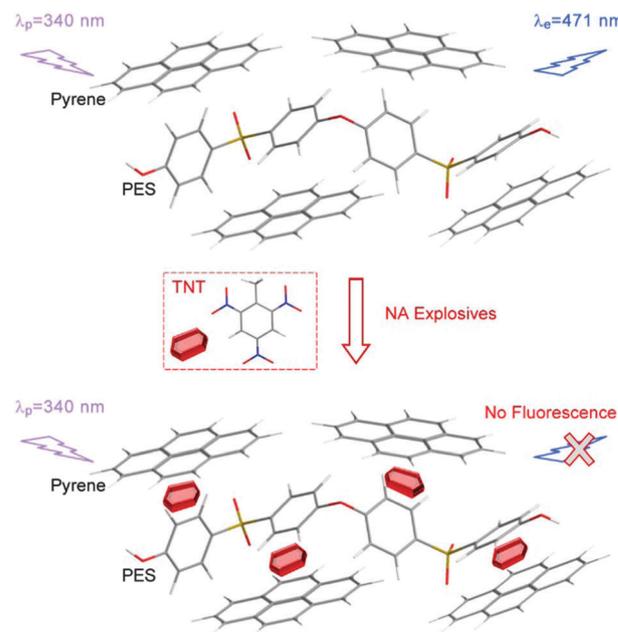
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A novel sensing material based on pyrene doped polyethersulfone worm-like structured thin film is developed using a facile technique for detection of nitroaromatic explosive vapours. The formation of π - π stacking in the thin fluorescent film allows 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 excited state of pyrene due to their low LUMO energies and as a result the fluorescent film is quenched¹⁸ (see details in ESI†).

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† 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

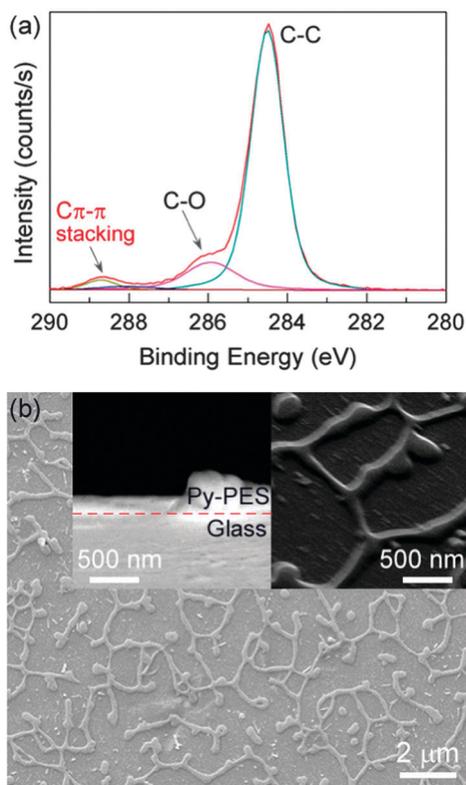


Fig. 1 (a) The C1s XPS spectra; (b) SEM image of the Py-PES thin film (top left inserted image; cross-section and top right inserted image; 30° tilted version of the same surface).

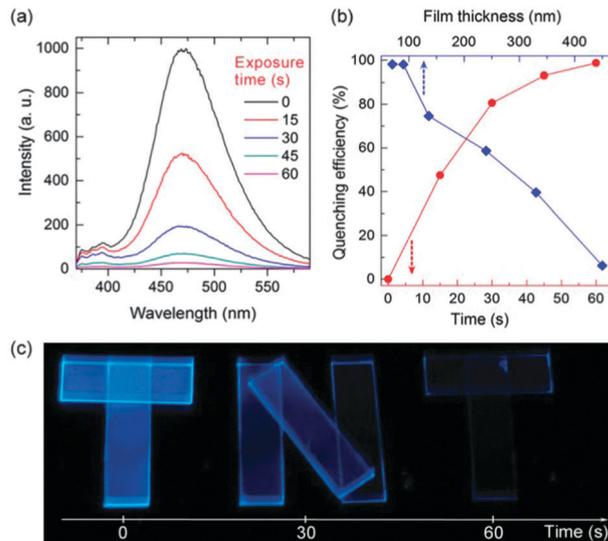


Fig. 2 (a) The time-dependent fluorescence intensity of Py-PES thin film upon exposure to equilibrium TNT vapours; (b) the quenching efficiency of Py-PES films with changing time and film thickness (red line indicates the quenching efficiency of 90 nm PES film); (c) photograph of Py-PES thin films under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

to 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).

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.

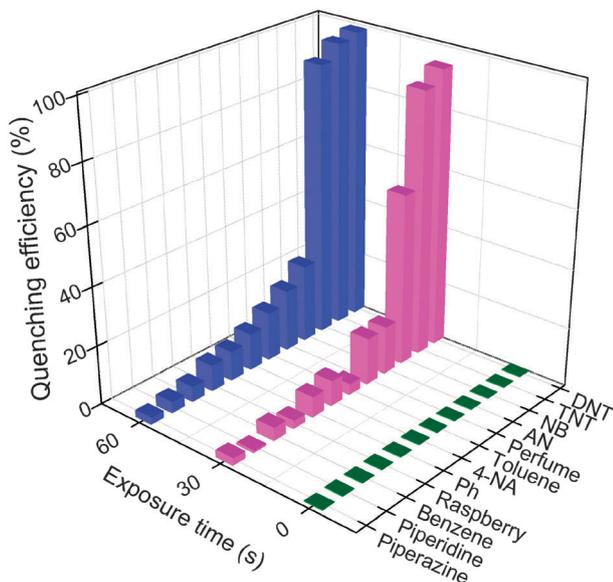


Fig. 3 The time-dependent fluorescence quenching efficiencies at 471 nm for saturated vapours of different chemicals on Py-PES thin films.

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.

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Supplementary Information

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

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Materials

Polyethersulfone (PES) was purchased from Ajedum, USA. Tetrahydrofuran (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 μ L) on glass slides (2.5 cm \times 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 compounds (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 pseudopotential with plane-waves up to an energy of $E_{\text{cut}} = 25$ 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 Zunger⁵ 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.

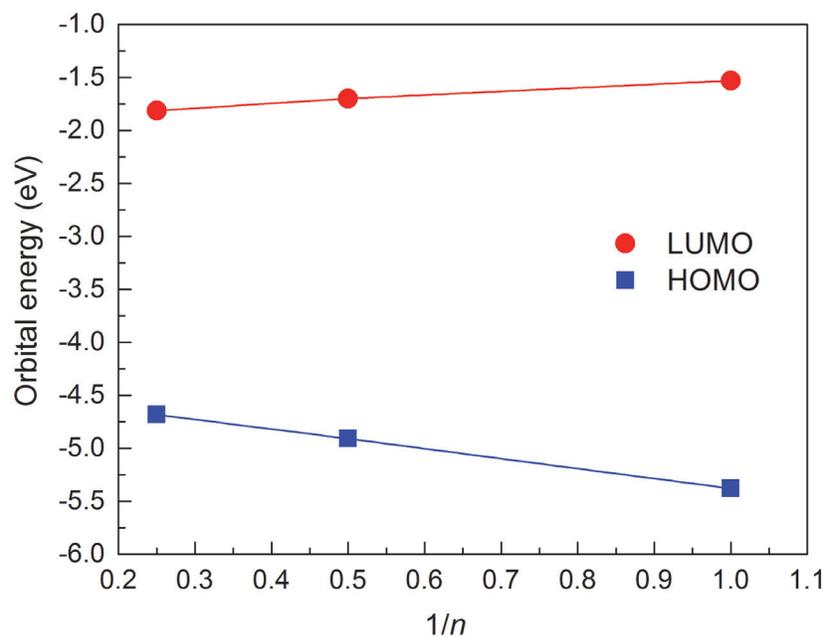


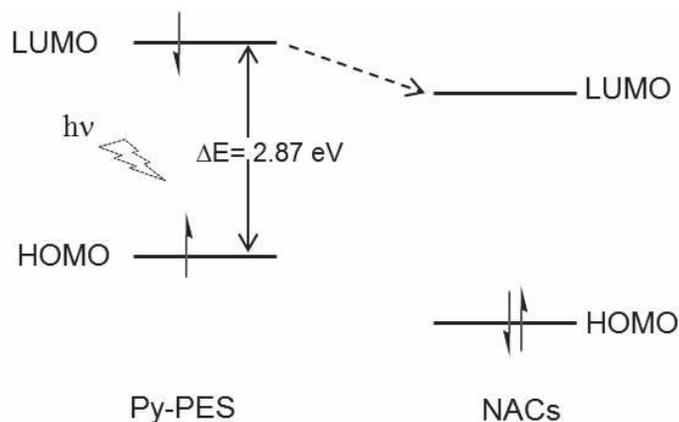
Fig. S1 Plots of the HOMO and LUMO energies of PES as a function of the repeat monomer units.

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 excited 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.

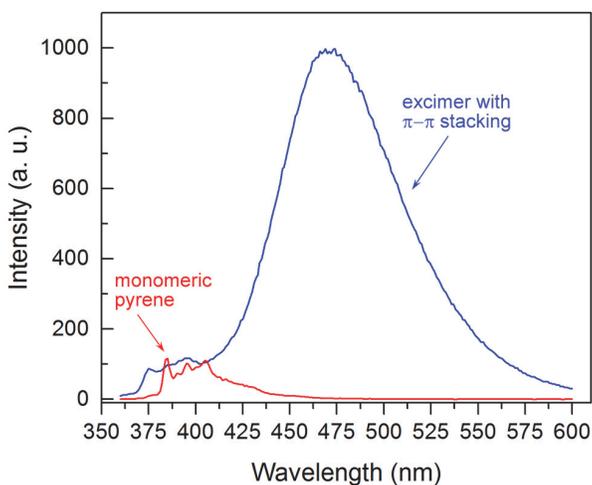


Fig. S2 The emission spectrum of Py-PES thin film with and without π - π stacking formation.

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.

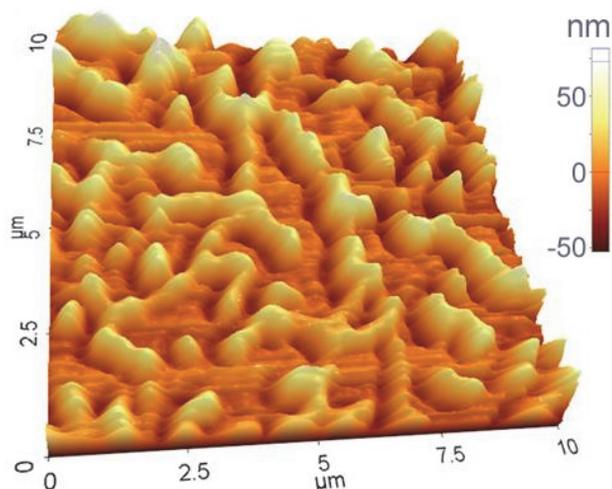


Fig. S3. 3D-AFM image of Py-PES worm-like structured thin film. The AFM image was collected in tapping mode for 10x10 μm area.

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