

Plasma deposition of perylene-adamantane nanocomposite thin films for NO₂ room temperature optical sensing

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ABSTRACT

This work reports the preparation, by a new remote assisted plasma deposition process, of luminescent nanocomposite thin films consisting of an insoluble organic matrix where photonically active perylene molecules are embedded. The films are obtained by the remote plasma deposition of adamantane and perylene precursor molecules. The results show that the adamantane precursor is very effective to improve the perylene-adamantane nanocomposite transparency in comparison with plasma deposited perylene films. The plasma deposited adamantane films have been characterized by secondary ion mass spectrometry and FT-IR spectroscopy. These techniques and atomic force microscopy (AFM) have been also used for the characterization of the nanocomposite films. Their optical properties (UV-vis absorption, fluorescence and refractive index) have been also determined and their sensing properties towards NO₂ studied. It is found that samples with the perylene molecules embedded within the transparent plasma deposited matrix are highly sensitive towards this gas and that the sensitivity of the films can be adjusted by modifying the aggregation state of the perylene molecules, as determined by the analysis of their fluorescence spectra. By monitoring the fluorescence emission of these films it has been possible to detect a NO₂ concentration as low as 0.5 ppm in air at room temperature. Due to their chemical stability and transparency in the UV-region, the remote plasma deposited adamantane thin films have revealed as an optimum host matrix for the development of photonically active composites for sensing applications.

KEYWORDS

Perylene dye, nanocomposite, optical sensors; NO₂ monitoring; fluorescence; plasma polymerization, adamantane thin film, high refractive index organic films.

1. INTRODUCTION

Perylene and perylene derivatives are polycyclic aromatic hydrocarbon dyes which are being used for the development of a wide range of semiconductor and optoelectronics devices, such as field effect transistors,^{1,2} supramolecular structures,^{3,4} solar cells,^{5,6} liquid crystal displays⁷ and organic light emitting diodes.^{8,9} Their use for the development of a NO₂ optical dosimeter for the remote monitoring of the degradation of high explosive materials (explosives, fuels, etc.) has been also claimed.¹⁰ In this context, we have recently reported a new kind of remote plasma polymer thin films that constitute a very good choice for the development of integrated photonic gas sensors of this compound.¹¹ Plasma polymerization is a very well-established synthetic procedure whereby the fragments produced by the decomposition of a volatile organic or organometallic molecule interacting with a glow discharge are bonded and recombined in a thin film. The nature of these so called *plasma polymers* is very different to a conventional polymer. As a general characteristic, the molecular structure of a precursor molecule is not maintained in the plasma polymers and the identification of the molecular composition of the starting monomer is not always straightforward by a simple chemical characterization of the films. This difficulty stems from the fact that the nature of the plasma polymer is mainly determined by the deposition conditions and much less by the chemical composition of the precursors. More recently, many authors have attempted to maximize the incorporation in the films of specific molecular groups from a monomer (i.e., amine, carbonyl groups, etc.) by different strategies involving the use of pulsed plasma discharges, high deposition pressures, low plasma power, etc. Most part of these investigations has been successfully focussed in the production of functional films, functional surfaces and plasma modification of commercial polymer surfaces for biomedical applications.¹²⁻¹⁴

In several recent works we have reported about a new remote plasma (RP) assisted process enabling the fabrication of highly luminescent polymeric thin films where a high concentration of dye molecules remain intact within a matrix formed by molecular fragments of the same dye generated by interaction

with a remote microwave plasma discharge.^{11,15-18} The procedure is based in the control of the interaction of sublimated dye molecules with the boundary region of the RP discharge. Up to now, this method has been applied to prepare optically active thin films of rhodamine 6G,^{15-17,19} ethyl red,¹⁶ 3-hydroxyflavone^{18,20} and perylene dyes.¹¹ In this latter case, although the obtained films revealed themselves as good optical sensors of NO₂, limits were found in the detection sensitivity and in their integration feasibility together with photonic structures due to a reduced capability to significantly vary their optical properties. In the present work, we explore a modification of this controlled plasma polymerization method by essaying the simultaneous remote plasma deposition (RPD) of two molecules, perylene and adamantane. A first purpose of this work is the fabrication of nanocomposite thin films where an optically active molecule (i.e. perylene) is embedded within a transparent polymeric matrix. This approach is common by other techniques of fabrication based on wet routes.^{10,21}

Adamantane was chosen to create a transparent nanocomposite matrix because it is a volatile organic molecule with single C-C bonds that, as shown in the next sections, has demonstrated to be very effectively plasma polymerized under remote conditions. Adamantane is a stable and very easy to handle solid state precursor. The RPD films are highly transparent presenting very low levels of conjugation (i.e., low absorption in the UV) and without the yellowish color typical of hydrocarbon plasma polymers resulting from the absorption in the high energy region of the visible spectrum.²² The fabrication of such transparent, mechanically stable and insoluble organic matrices by remote plasma deposition is one of the achievements of this work. It is important to notice that due to the relatively high vapor pressure of this compound, highly cross-linked adamantane plasma polymers are also obtained in zones of the reactor in contact with the plasma. On the contrary, the perylene containing films are only obtained in the sample holder placed in front of the organic evaporator cell.

This work aims at the development of perylene containing organic layers for the fabrication of photonic NO₂ dosimeters or active luminescent layers for the development of photonic sensing devices. To achieve this goal it is required to primarily get a very precise control over the thin film composition and structure defining thin films with customized values of n and k. Secondly, to optimize the NO₂

sensing interactions, it is also required to have a strict control over the molecular dispersion of the dye molecules within the film structure. These two requirements are also needed for the integration of these organic films as active component in photonic structures, prior to be assembled into photonic sensing devices.¹⁸ The last section of the paper consists of several examples that demonstrate the possibility of using the studied films as room temperature sensor of very low concentrations of NO₂ in air.

Results concerning the properties of film using perylene as unique precursor have been recently published.¹¹ In the present work we report a description of the deposition technique and of a variety of perylene-adamantane thin film materials that can be obtained by the RP assisted vacuum deposition technique. We also describe their structural and their functional optical properties associated with the UV-vis absorption and fluorescence emission of the embedded perylene molecules. Specific attention is also paid to the characterization of the plasma deposited adamantane films. Finally, the sensing properties towards NO₂ of the perylene-adamantane composite films have been addressed by following the changes in the fluorescence emission of the films as a function of the exposure time. The obtained results have shown that for certain family of perylene-adamantane films, the sensitivity can be highly enhanced to detect very low concentration of this gas in air. This work opens the possibility of obtaining new families of organic luminescent nanocomposite thin film materials with customized optical and luminescent properties.

2. EXPERIMENTAL METHODS

Perylene (C₂₀H₁₂, (dibenz[d,k]anthracene)) (P) and adamantane (C₁₀H₁₆, (tricyclo[3,3,1,1]decane)) (A) solid powder were purchased from Sigma Aldrich and used as received.

2.1 Plasma Procedure. A general scheme of the experimental setup used for deposition of dye containing thin films is presented elsewhere.¹⁶ In resume, this experimental set up allows controlling the interaction between the plasma species and the evaporated precursor molecules in order to regulate the

fragmentation degree of the evaporated dye molecules arriving to the substrates. Thus, by adjusting the applied MW power, the pressure during the discharge and/or the distance between the substrate and the plasma region, it is possible to grow organic thin films containing a controlled amount of integer and optically active dye molecules.^{15,16} The experimental conditions for the preparation of RPD perylene thin films have been published recently.¹¹ As a difference, in this work we study the properties of films deposited from perylene and adamantane.

The experimental system consists of a vacuum chamber with two zones for the plasma and for the remote deposition. A set of magnets surrounding the chamber sustains an Argon (Ar) discharge in the plasma region under microwave electron cyclotron resonance (ECR) conditions. The microwave is applied to the plasma chamber through a flat Pyrex window. A set of Knudsen cells are placed in the deposition zone in order to sublime the dye onto the substrates localized in the downstream region of the plasma discharge, at 5 cm from the plasma region. Additionally, an external and heatable glass ampoule containing adamantane powders is connected to the deposition chamber in order to supply a regulated vapor pressure of this compound inside the reactor. The microwave power was varied in the range 150 - 300 W, and the argon pressure was varied in the range 1×10^{-1} to 1×10^{-3} mbar. The pressure of the system was controlled by a conductance control valve controller connected to a motorized valve and a capacitance pressure gauge (Baratron). Ar plasma gas is dosed to the plasma chamber using a calibrated mass flow controller (MKS). The system was pumped before and after deposition with a turbomolecular pump to reach a base pressure of 10^{-6} mbar. The RPD perylene-adamantane (PA) thin films were prepared by dosing a given vapor pressure of adamantane and sublimated dye molecules into the downstream region of an Ar microwave ECR plasma. Pure adamantane (RPD-A) and perylene (RPD-P) remote plasma deposited films were also grown in the same manner by only dosing one of the two precursor molecules into the deposition zone. Additionally, reference perylene and adamantane films were obtained by sublimation in absence of plasma discharge. Film thickness and deposition rate were controlled by using a quartz crystal monitor placed beside the

sample holder in the deposition region. Typical growing rates between 1 and 3 nm/min were achieved by controlling the heating of the Knudsen cells and the adamantane dosing system.

2.2 Sample Preparation. Different perylene-adamantane plasma deposited thin films have been prepared by continuously dosing into the chamber a given vapor pressure of adamantane, while opening and closing a shutter in the perylene Knudsen cell for fixed periods of time. During the synthesis of the PA layers the relative deposition rates of A and P were controlled by both heating the adamantane container and dosing line at different temperatures to increase the vapor pressure of this compound and by changing the heating temperature of the perylene cells. The investigated samples are summarized in Table 1 where we indicate the ratio between the deposition rates of perylene and adamantane as measured with a quartz crystal monitor. In this table, a qualitative assessment of the dye concentration in the films has been included as the perylene dye absorption at $\lambda = 440$ nm determined after background removal. For samples PA-0.5 to PA-1.5 the deposition rate of adamantane was 0.2 \AA s^{-1} and the perylene cell was maintained open for a deposited film thickness of 50 \AA and closed at regular intervals for a deposited film thickness of 25 \AA . Note that for sample PA-3 the deposition rate of adamantane was 0.1 \AA s^{-1} and the deposition of perylene was not interrupted by the shutter. The total thickness of the PA films was 150 nm comprising a first layer of A of ~ 20 nm thick. Other studied thin films are pure adamantane and perylene plasma deposited films and sublimated layers. The perylene plasma polymeric sample has been incorporated in the study only for comparative purposes as a complete study about its synthesis and characteristics can be found in a previous publication.¹¹ The films were deposited on polished fused silica plates (1 mm thick) and on silicon (100) wafers. Frosted glass substrates were used in some experiments aiming at increasing the sensitivity to NO_2 by increasing the thin film surface area.

2.3 Thin Film Characterization. The mass spectra of the samples were recorded on a time-of-flight secondary-ion mass spectrometry (TOF-SIMS) IV instrument from Ion-ToF GmbH Germany. The

sample was bombarded with a pulsed bismuth ion beam. The generated secondary ions were extracted with a 10 kV voltage and their time of flight, from the sample to the detector, was measured in a reflectron mass spectrometer. Typical analysis conditions in this work were 25 keV pulsed Bi⁺ beam at 45° incidence rastered over 500 × 500 μm². An electron flood gun for charge compensation was used during the measurements. The intensities of these signals have been normalized to the total intensity of the spectrum. Fourier transform infrared (FT-IR) spectra were collected in transmission mode in a Nicolet 510 spectrometer and using Si (100) substrates to collect the background signal.

Noncontact atomic force microscopy (AFM) measurements were carried out with a Cervantes AFM system from NANOTEC using commercial noncontact AFM tips from MikroMasch.

Field Emission Scanning Electron Microscopy (FESEM) images of samples deposited on Si (100) were recorded using a Hitachi S-4800 FESEM microscope.

UV-vis transmission spectra were collected in a Varian Cary 300 spectrophotometer for samples deposited on polished fused silica slides. The optical properties of the thin films deposited on Si (100) have been measured with a variable angle spectroscopic ellipsometer (VASE) from J.A. Woollam Co., Inc. Values of Δ and Ψ were obtained over the spectral range of 300 to 1200 nm, at 1 nm resolution. Measurements were performed at three different incidence angles: 65°, 70° and 75°. Optical modeling and parameters fitting were done with the WASE32 program (J.A. Woollam Co., Inc.). In order to model the ellipsometric spectrum with fixed thickness (thickness values were obtained by transversal FESEM images) non-ideal model options were applied such as: film thickness, non-uniformity and angular spread of the beam entering into the detector; also some fit parameters were coupled and limited. On the other hand, neither non partial polarization effects nor monochromator bandwidth effects were found. The data were analyzed assuming the Cauchy dispersion law (non-absorbing region) and an ensemble of three Lorentz oscillators (absorbing region). The quality assessment of the fit data was performed by using the mean-squared error (MSE) value. A small MSE implies that the assumed model was appropriate. MSE was below 10 units for our samples in the absorbing region and below 5 in the transparent region.

The thickness of the films has been obtained by transversal FESEM micrographs and also measured with a Mahr Surf XR-20 profilometer. Similar results were obtained by VASE for samples deposited on Si(100).

Fluorescence analysis were conducted in a Jobin-Yvon Fluorolog3 spectrofluorometer operating in the front face mode and using grids of 2 and 3 nm for the excitation and emission, respectively. The fluorescence spectra were excited with radiation of 412 nm for the perylene-adamantane RPD films and perylene solution; and with radiation of 390 and 420 nm for the perylene sublimated layer and the perylene RPD film, respectively.

The evolution of the fluorescence spectra of samples exposed to NO₂ were measured in a steel chamber connected to the spectrofluorometer by a set of optical fibers. A flow of 500 ppm of NO₂ (500 ppm/air) was mixed with a regulated industrial air flow to achieve the desired NO₂ concentrations of 5 and 0.5 ppm at atmospheric pressure. In these experiments the detection limit has been estimated as the shorter exposure time for which emission intensity fulfill the condition $I < (\bar{I}_i - 3S_B)$.²³ The mean value \bar{I}_i and the standard deviation S_B have been determined from a set of 20 measurements conducted before the NO₂ exposure experiment, using the same sample and an industrial air flow.

For the fluorescence analysis, the films were deposited on polished fused silica slides, while for fluorescence sensing studies the films were deposited in polished fused silica and also in frosted fused silica substrates. These latter substrates have a high surface roughness determined by profilometry (Ra=0.44 μm) in comparison with the polished fused silica slides (Ra<0.01 μm).

The solubility of the thin films was tested by immersing a set of them in water, ethanol and toluene for a period of 12 hours at room temperature. After each immersion test the films were dried in flowing nitrogen for two hours. Temperature stability tests were carried out in a tubular oven in Ar flow at atmospheric pressure. The films were heated during 4 hours at 150, 200 and 250 °C.

3. RESULTS AND DISCUSSION

3.1 Thin film characterization. Adamantane, perylene and adamantane-perylene RPD thin films according to our experimental technique renders very stable and homogenous thin films. All of them were insoluble in water, ethanol and toluene solvents and thermally stable up to 250°C. In addition, no evidence of aging of the studied films has been detected after dark storage in a laboratory environment free of NO₂ for a period of more than one year.

To assess the structural characteristic of the adamantane and perylene-adamantane remote plasma deposited films we have investigated these samples by ToF-SIMS. Perylene sublimated samples have been also measured as reference. Sublimated adamantane samples are not stable under the ion beam of the ToF-SIMS spectrometer being very rapidly sublimated. For this reason, adamantane mass spectrometry data from the bibliography will be used as reference.²⁴

Figure 1a shows ToF-SIMS spectrum corresponding to a film of adamantane (RPD-A sample). This spectrum is characterized by a series of intense peak groups in the region $m/z < 100$ being the more intense peaks centered at $m/z = 41, 55, 67, 77$ and 91 . Additional peaks with smaller intensity are also observed for m/z in the range between 100 and 250. Some small contribution can be observed at m/z at around 135 at the position where the most intense peak of adamantane (Adamantane $M^+ - H^+$ molecular ion) is detected by conventional mass spectrometry of this molecule (molecular weight of adamantane 136.23 u) and at $m/z = 136$ (Adamantane M^+).²⁴ The intensity of the peaks in the spectrum indicates that in the RPD films hydrogenated fragments with 2, 3, 4, 6 and 7 carbon atoms are relatively abundant. This result very likely supports the fragmentation of the adamantane molecule during the thin film deposition to form a solid organic film. Note that in this case some fragmentation produced by the ion beam during the measurement cannot be discarded. In addition, several peaks like those at $m/z = 105, 121$ and 165 and other small peaks visible for $m/z > 100$ are compatible with a partial oxidation of some of these fragments (e.g., like in $C_7O_2H_5$ fragments) or the formation of bigger carbon aggregates than in the precursor molecule suggesting the incorporation of some oxygen to the film and/or the formation of fragments bigger than the precursor (non-polymerized) molecule. The first possibility agrees with

previous results dealing with the partial polymerization of different dye molecules where we could detect by X-ray photoemission spectroscopy the incorporation into the film of some oxygen from the residual impurities of the chamber.^{11,15-17} In any case, the detection of large molecular fragments agrees with the existence of relatively long C_nH_m chains in the RPD film.

Figure 1c shows a ToF-SIMS spectrum of a RPD-P film and Figure S1 (Supporting Information) shows the spectrum of a sublimated perylene film. Both spectra are included here to be used as references for the analysis of the PA samples. The ToF-SIMS spectra of the RPD-P films show that these samples are formed by an organic matrix of perylene fragments, where some low intensity peaks corresponding to integer perylene molecules embedded in the film can be detected. The most intense features of these spectra (e.g. spectrum RPD-P) were the fragments in the $m/z < 100$ region. Note in the figure that many additional fragments at $m/z > 100$ have an intensity comparable or higher than that of the perylene molecular ions peaks at $m/z = 252$ and 253 . In contrast, the spectrum of the sublimated perylene film measured under the same experimental conditions is mainly dominated by the perylene molecular ion peaks. The comparison of the two ToF-SIMS reference spectra indicates that the fragments measured in the plasma films can be attributed to the dye fragmentation and the formation of a solid matrix during the plasma deposition process¹¹

Figure 1b shows the spectrum corresponding to a perylene-adamantane film (sample PA-3). The regions corresponding to the adamantane and perylene molecular ions can be observed in detail in Figures 1d and 1e, respectively. In these graphs it is possible to observe the main molecular ions of the two different components: $C_{10}H_{16}$ (Adamantane M^+ at $m/z = 136$), $C_{10}H_{15}$ (Adamantane $M^+ - H^+$ at $m/z = 135$), $C_{20}H_{12}$ (Perylene M^+ at $m/z = 252$) and $C_{20}H_{13}$ (Perylene M^+H^+ at $m/z = 253$).²⁴ The more intense peaks are in the region of $m/z < 150$ consisting in fragments that are related with the perylene and adamantane molecules many of them containing oxygen. Thus, the interpretation of the ToF-SIMS results in the perylene-adamantane system is very similar to what has been discussed previously for the perylene and adamantane plasma homopolymers. In this case, the results indicate that the films are obtained by a plasma fragmentation process involving the two molecules.

The ToF-SIMS analysis indicates that the introduction of the adamantane monomer permits to fabricate a plasma film where integer perylene molecules are present. On the other hand, this analysis also demonstrates the presence of a low percentage of integer adamantane molecules in the RPD-A and PA films. This result is a good example of the capacity of the remote reactor design to regulate the interaction of the plasma with the species arriving to the surface and with the surface of the growing film in the remote position. It is interesting to note that the adamantane is introduced in the form of a vapor in the chamber and is not confined to the remote region as occurs with the dye that is sublimated toward a substrate. Therefore, simultaneously with the deposition of the perylene-adamantane films adamantane plasma polymers are deposited in zones of the reactor that are closer to the plasma discharge and in any surface in contact with the plasma.

The organic films deposited by the remote plasma assisted vacuum deposition technique are formed by the condensation and surface reaction of reactive fragments of the dye molecule. In these films the fragmentation process is not complete and a percentage of integer dye molecule are also embedded within the solid matrix. As the plasma interaction is more effective, the number of non-fragmented dye molecules is reduced.¹⁵⁻¹⁷ These general structural characteristics have been previously proved by UV-vis spectroscopy, FT-IR and other techniques in several systems including the plasma assisted deposition of perylene films.^{11,15-17} Perylene-adamantane plasma deposited films bring about a new variable with respect to simple films where the plasma interaction affects exclusively to one type of organic precursor molecule. The PA thin films are formed by the interaction with a remote plasma of two different molecules and their fragments: adamantane which produces a passive transparent organic matrix and perylene which, even if partially contributing to the formation of the matrix, becomes integrated into the film as a photonic active component.

Figure 2 shows a series of FT-IR spectra recorded for the films RPD-P, RPD-A, PA-1 and PA-3. Spectra recorded for sublimated perylene and adamantane molecules are included for comparison. Assignment of the bands in the FT-IR spectra has been done according to the bibliography.²⁵⁻³⁰ Spectra of sublimated perylene and sample RPD-P have been reported previously in a work on perylene plasma

polymers.¹¹ The FT-IR spectrum of sublimated perylene layer is dominated by two bands at 764 and 810 cm^{-1} attributed to C-H out-of-plane bending vibrations. Other less intense bands can be also observed in the region from 1100 to 1700 cm^{-1} that have been assigned to C-H in-plane bending, ring stretching, C=C aromatic stretching and C=O stretching vibrations. The spectrum of the RPD-P thin film reproduces most of these bands, sometimes with some small displacements in position and, in all cases, an appreciable broadening. From all these bands, those at 764 and 810 cm^{-1} can be considered as a fingerprint of perylene molecules and related molecular fragments in the films. These bands are more intense in sample RPD-P than in the PA samples. In addition, the spectrum of the RPD-P film presents a broad band at approximately 3450 cm^{-1} attributed to –OH groups and several better resolved bands at around 2900 cm^{-1} due to –C-H stretching vibrations. As previously mentioned, the development in our films of bands due to –OH and –C=O groups responds to a common phenomenon in most plasma deposition processes by which the residual oxygen and/or water molecules in the chamber, even if in very small concentrations (e.g., lower than 10^{-5} mbar in our case), become plasma activated and react with the fragments of the monomer.^{12,13,31,32} The oxygen content has been also ascribed to post-deposition reactions of trapped radicals and O_2 .^{12,13}

For sublimated adamantane, most characteristic bands, attributed to –C-H vibrations, appear at around 2900 and 1500 cm^{-1} . The spectrum of sample RPD-A also shows these two vibrational features but with an appreciable broadening. Thus, the vibrational features around 2900 cm^{-1} are forming a single broad band in the plasma deposited sample. In addition, another band at around 1700 cm^{-1} due to –C=O stretching vibration develops in this sample.

Samples PA-1 and PA-0.5 (not shown in the figure) present FT-IR spectra very similar to the one corresponding to sample RPD-A. This means that the dye fragments and molecules incorporated within the plasma film are quite diluted, so that no vibrational bands of the formers are distinguishable in the spectrum. In sample PA-3 (and to a much lesser extent in sample PA-1.5, not included in the figure) the fingerprint bands of perylene at around 800 cm^{-1} are visible in the spectrum what is congruent with the higher perylene deposition rates used in the synthesis.

The observed broadening of the IR band of the perylene and perylene-adamantane plasma films in comparison with the spectra of the sublimated layers can be attributed to structural disorder in the films. This broadening has been also ascribed to the complete or partial hindering of vibrational modes due to the plasma fragmentation of precursors and the formation of a cross-linked polymeric structure.^{12,13,31,32} The FT-IR analysis of the perylene-adamantane RPD films indicates that these films are formed by integer molecules and by molecular fragments of the two precursors. However, from this analysis it cannot be inferred whether the structure of the films consists of molecular fragment aggregates or is a cross-linked polymeric network.

The AFM analysis of the surface topography of the PA samples (Figure 3) indicates that in all cases, the films are very flat, with estimated RMS roughness values in the order of 0.3 nm for ~150 nm thick films. These low RMS roughness values have also been recently founded in perylene plasma films¹¹ and in other polymeric thin films deposited in a similar experimental set-up.¹⁷⁻¹⁹ The surface topography images and lineal profiles of the prepared samples are rather similar independently of the perylene/adamantane ratio indicating that the surface roughness is not affected by the codeposition process. It is important to stress that the RMS roughness values obtained are exceptionally low and among the best reported for thinner optical films prepared by plasma polymerization.^{33,34} The high planarity of these films is a very important characteristic for obtaining films for photonic applications, ensuring the absence of light dispersing features in the films. The results of the FESEM characterization of the films are congruent with the AFM analysis. No defined features, cracks, voids or aggregates can be observed in the film surfaces for both low and high magnifications. The cross-section of the films also looks homogeneous and smooth to the microscope as can be observed in the example of Figure S2 corresponding to a PA sample (see supporting information file).

The results of the thin film characterization provide a partial description of the thin film microstructure. The use of additional analytical techniques like nuclear magnetic resonance (NMR) spectroscopy is hindered due to the amount of material required for the analysis and the insolubility of films. This limitation is common to films deposited by plasma polymerization.¹³ In addition, the

relatively simple bond structure of the perylene and adamantane precursors and of the resulting plasma deposited films, mainly consisting in C-C single and double bonds, preclude that the FT-IR analysis of the films gives direct evidences of the formation of a plasma polymeric cross-linked structure. The AFM and FESEM analysis showed that the plasma films are homogenous and do not contains crystallites or aggregates that are typical of room temperature sublimated organic films. Besides, the solubility tests indicate that the perylene molecules are embedded in a solid organic matrix that prevents the dye to be in contact with solvents (including toluene in which perylene is highly soluble). In addition, the films are thermally stable at least up to 250°C, much higher than the sublimation temperatures of the adamantane and perylene precursor molecules that are around 40 and 150 °C, respectively. All these findings indicate that the plasma deposits are not formed by low molecular weight fragments weakly associated by Van der Waals forces and are consistent with a description of these films as tridimensional cross-linked plasma polymers with a percentage of embedded integer molecules.

3.2 Optical properties of the nanocomposite thin films. Figure 4 shows a series of transmission spectra of PA, RPD-P and RPD-A thin films grown on fused silica with thicknesses of ~150 nm. The figure also includes the transmission of the fused silica substrate as well as the spectrum of a sublimated layer of perylene. This latter spectrum consists of a broad absorption band that starts at ~300 nm and extends through the whole visible region. In contrast, the spectra of the PA thin films depict well defined bands at 398, 420 and 445 nm. The closer look to these bands, reported in an absorbance scale in the inset in this figure, shows that their shape is similar to that of isolated molecules of this dye in solution.³⁵⁻³⁷ In this inset, it is also apparent that the band intensity follows a parallel progression to the nominal concentration of dye molecules in the films (cf. Table 1). This evidence proves that the utilized method of preparation of dye thin films provides a rather strict control over the concentration of integer molecules of perylene present in the samples. These molecular bands are superimposed on a decaying background extending to the UV region of the spectra that differs according to the plasma film compositions. While in the RPD-P film the absorption background extends to the visible zone of the

spectrum, in the PA films this feature is more confined towards the UV zone for $\lambda < 405$ nm. It is also remarkable that the transmittance spectrum of the RPD adamantane film (RPD-A) defines a very flat high transmittance in the spectral region extending from ~ 300 to 900 nm while a similar decrease in transmittance is observed but shifted to lower wavelengths ($\lambda < 270$ nm).

The observed thin film absorptions in the UV region can be attributed to the presence of conjugated unsaturated bonds in the films.³⁸⁻³⁹ Thus, these decreases in transmittance are in part very likely due to the presence of unsaturated fragments of the perylene dye in the PA and RPD-P films. However, this type of absorption curves are also a characteristic of conjugated bonds typically observed in cross-linked polymeric structures obtained by plasma polymerization of organic precursors.³⁹⁻⁴⁰ In fact, this absorption background is also present in the transmission spectrum of the RPD-A film although shifted to lower wavelengths. This result evidences that unsaturated conjugated carbon bonds are also a result of the precursor fragmentation process produced by the remote plasma.

To our knowledge, plasma polymerized adamantane thin films have not been reported in the literature as a matrix for the development of composite optical thin films. In this regard our data suggest that, due to its extraordinary high transmittance in all the visible range and stability in air this type of polymeric matrix can be of the outmost interest for the preparation of photonic nanocomposite thin films.

Despite the similar shape of the absorption bands presented by all the RPD perylene films, their fluorescence spectra change with the concentration of perylene. Figure 5a shows a series of fluorescence spectra for the different PA films and for a 10^{-6} M toluene solution of perylene which is included for comparison. This latter spectrum is characteristic of isolated molecules of this compound with typical bands appearing at 442, 471 and 502 nm.^{35,41,42} It is remarkable that the fluorescence spectrum of sample PA-05 depicts a series of bands with similar shape, position and relative intensity than those of the perylene solution taken as a reference. These bands are broader and appear superimposed on a decaying background or broad band contribution extending up to 650 nm. The spectra of samples PA-1 to PA-3 depict the same bands found in the perylene solution, although they are broader and present a different relative intensity. (i.e., the band around 475 nm is now the highest one in detriment of the band

around 450 nm). A comparison of these fluorescence bands with those of sample RPD-P and a sublimated layer of perylene (cf. Figure 5b) provides some insights about the evolution of the overall spectral shapes. From this comparison, it is apparent that the spectra of samples PA-1 to PA-3 are the result of the superposition of contributions of both isolated molecules embedded within the film and interacting molecules in associated states which resemble those existing in the polymerized RPD-P film and the evaporated perylene layer. In solution and other highly concentrated systems shift/broadening of fluorescence bands have been interpreted as due to the interaction between perylene molecules.^{35,41-43} Admitting a similar interpretation for our results, the found tendency suggests that in sample PA-0.5 the perylene molecules are isolated and do not interact between them. As the concentration of perylene increases towards sample PA-3, interactions between molecules develop. Therefore, a reasonable working hypothesis is that while in sample PA-0.5 most molecules are isolated, in sample PA-3 we have clusters or associations of perylene molecules with a configuration relatively similar to that existing in the RPD-P samples. The similar shapes of the excitation spectra of perylene in solution and in sample PA-05, provided as supporting information (Figure S3), give more credit to this assumption.

Plasma polymeric thin films have been extensively studied for optical applications. Apart from the mechanical and chemical robustness of the plasma polymers the plasma polymerization technique permits to control the refractive index of polymeric films in a relatively wide range as a function of the plasma conditions,^{12,44-46} by changing the gas plasma composition²² or copolymerizing controlled percentages of two monomers,¹⁷ typically hydrocarbon and fluorocarbon monomers being the lower refractive index obtained as the percentage of the latter increases.⁴⁷

The perylene containing thin films studied in this work are intended to be integrated in photonic structures for the development of photonic sensors. For this application it is critical the control of the optical properties of the films. Figure 6 shows the refractive index curves of samples RPD-A, PA-0.5, PA-1.5, PA3 and RPD-P determined by variable angle spectroscopic ellipsometry. The results indicate the refractive index can be tailored as a function of the perylene content for films deposited in similar plasma conditions. Note all the values reported for PA films are obtained by using similar plasma

conditions but changing the perylene concentration in the films. The value of n increases gradually as the dye concentration in the films increases. Thus, the lower values correspond to the adamantane sample (RPD-A) with $n_{589\text{nm}} = 1.56$ ($n_{632.8\text{nm}} = 1.56$). The refractive index reaches a value of $n_{589\text{nm}} = 1.70$ ($n_{632.8\text{nm}} = 1.69$) for sample PA-3 and $n_{589\text{nm}} = 1.78$ ($n_{632.8\text{nm}} = 1.76$) for the RPD-P sample. At the higher dye concentrations studied the films have relatively high refractive indices when compared with plasma polymers^{44,45,47} or even with conventional polymeric optical films.⁴⁸ These high refractive index values are slightly higher than those reported for polymetalocene films,⁴⁹ plasma polymerized ferrocene thin films,⁴⁶ and close to values reported for some diamond like coatings.⁴⁴

3.3 Sensing response towards NO₂. In a previous work, we have shown that NO₂ is able to diffuse through a polymeric thin film of type RPD-P, inducing changes in its UV-vis absorption spectrum, refractive index and a quenching in luminescence that were dependent on the exposure time to this gas.¹¹ These effects are attributed to the formation of non-fluorescent nitro-perylenes by a selective reaction of NO₂ with perylene.^{10,11} Since the incorporation of NO₂ into the films is not reversible at room temperature, these films can be used for developing accumulative disposable NO₂ optical sensors. This kind of device has been proposed for the remote monitoring of the degradation of high explosive materials.¹⁰

In the perylene/adamantane films, the quest for NO₂ sensitive thin films requires as a condition that molecules of this gas may diffuse through the plasma polymeric film to reach the embedded perylene molecules, either isolated or in the form of small aggregates (i.e., as in samples PA-05 and PA-3, respectively). Figure 7a shows the time evolution of the fluorescence spectrum of sample PA-1.5F (F indicates the film have been deposited on frosted fused silica) exposed to a NO₂ concentration of 5 ppm in air at room temperature. It is clearly appreciable in this series of spectra that the fluorescence signal decreases significantly after 1h of exposure proving the high sensitivity of this film as an accumulative sensor of NO₂ and that the plasma polymeric film can be considered as a permeable and optically neutral matrix for the development of NO₂ photonic sensor materials. A similar behavior was found for

thin films with a relatively higher concentration of perylene, although the evolution of the fluorescence spectra presented differences for the most concentrated samples. This is clearly evidenced in Figure 7b showing the evolution of fluorescence intensity at $\lambda = 507$ nm for samples PA-3 and PA-1.5 exposed to an air flow with a NO₂ concentration of 5 ppm. The comparison of these evolution curves clearly supports the higher sensitivity of the PA-1.5 sample to small traces of NO₂. The smaller sensitivity found for samples with a higher concentration of perylene must likely be related with the formation of perylene aggregates in sample PA-3 and the fact that in diluted PA samples the dye molecules are isolated within the matrix. In this case, their fluorescence emission seems less affected by the nearby molecules but is effectively quenched when entering in contact with the NO₂. An enhanced sensitivity towards NO₂ can be achieved when the PA samples are deposited on frosted fused silica (e.g. sample PA-1.5F in Figure 7b). Thus, by depositing the film in this type of rough substrate the exposed thin film surface area is highly increased. It must be remarked that while transmission spectra are very much affected by the scattering of light passing through this rough substrate, its high roughness induces an increase in the apparent luminescence of the films. This factor also contributes to increase the signal to noise ratio and, therefore, the sensitivity of detection. The sensitivity enhancement is clearly appreciable when comparing the curve PA-1.5F with that of the PA-1.5 film in Figure 7b. Figure 7c shows the evolution of the luminescence response of a film PA-1F to a lower concentration of NO₂ of 0.5 ppm, a concentration similar to those detected in some traffic tunnels during rush hours.⁵⁰ From this experiment we have estimated a detection limit lower than 15 min for a 0.5 ppm NO₂ flow in air. Note that this dose is close to the risk level stated by the World Health Organization in 2001.⁵⁰

The previous results indicate that it is possible to regulate the sensitivity of the perylene containing polymers to this gas for room temperature accumulative NO₂ sensing in air. These films can be tailored to be used as dosimeters in scenarios with very high (i.e. high explosives or fuels storage facilities) or relatively low concentrations of NO₂ (i.e., road traffic tunnels).

4. Conclusions

The present work has shown that plasma deposited adamantane thin films present outstanding properties for the development of composite thin films where photonic active molecules such as perylene can be embedded. The partial plasma co-polymerization process utilized for the preparation of perylene-adamantane films provides a strict control over the optical properties of the films and particularly over their fluorescent behavior by just adjusting the concentration of entire perylene molecules. In this way, the prepared films, containing isolated and partially aggregated perylene molecules, depict the fluorescence spectra typical of isolated molecules of perylene in solution or a broaden shape attributed to the formation of aggregates of this molecule.

The perylene-adamantane films have revealed as promising materials for the development of accumulative sensors of NO₂. Particularly when detecting the fluorescence signal, it has been demonstrated that the films with isolated perylene molecules are capable of detecting very low NO₂ concentrations of 0.5 ppm in air and at room temperature with a detection limit < 15 min of exposure to a NO₂/air flow of 0.5 ppm. Moreover, by adjusting the perylene concentration within the composite films, it is possible to prepare a series of photonic sensors films with different sensitivities and, therefore, quite well adapted for detecting in different environments. It is also remarkable that for this sensing function, plasma polymerized adamantane films are ideal because they are optically neutral (i.e., thin films of this material are transparent in the visible) but NO₂ permeable, this latter characteristic being a requisite for the development of sensor films.

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Supporting Information Available. ToF-SIMS spectrum of a reference sublimated perylene thin films. Cross sectional FESEM micrograph of a PA sample deposited on Si(100). Excitation spectrum of

perylene-adamantane remote plasma deposited film (PA-0.5) compared with the excitation spectra of perylene-remote plasma deposited (RPD-P) and sublimated films and with that of perylene in a diluted toluene solution (10^{-6} M). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

- (1) Piliago, C.; Jarzab, D.; Gigli, G.; Chen, Z.; Facchetti, A.; Loi, M. A. *Advanced Materials* **2009**, *21*, 1573.
- (2) Briseno, A. L.; Mannsfeld, S. C. B.; Reese, C.; Hancock, J. M.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano Letters* **2007**, *7*, 2847.
- (3) Zhou, Z.; Brusso, J. L.; Holdcroft, S. *Chemistry of Materials* **2010**, *22*, 2287.
- (4) Borrás, A.; Aguirre, M.; Groening, O.; Lopez-Cartes, C.; Groening, P. *Chemistry of Materials* **2008**, *20*, 7371.
- (5) Breeze, A. J.; Salomon, A.; Ginley, D. S.; Gregg, B. A.; Tillmann, H.; Horhold, H.-H. *Applied Physics Letters* **2002**, *81*, 3085.
- (6) Nakamura, J.-i.; Yokoe, C.; Murata, K.; Takahashi, K. *Journal of Applied Physics* **2004**, *96*, 6878.
- (7) Kim, Y. D.; Kim, J. P.; Kwon, O. S.; Cho, I. H. *Dyes and Pigments* **2009**, *81*, 45.
- (8) Kim, C.-H.; Shinar, J. *Applied Physics Letters* **2002**, *80*, 2201.
- (9) Wu, C. C.; Lin, Y. T.; Chiang, H. H.; Cho, T. Y.; Chen, C. W.; Wong, K. T.; Liao, Y. L.; Lee, G. H.; Peng, S. M. *Applied Physics Letters* **2002**, *81*, 577.
- (10) Sasaki, D. Y.; Singh, S.; Cox, J. D.; Pohl, P. I. *Sensors and Actuators B: Chemical* **2001**, *72*, 51.
- (11) Blaszczyk-Lezak, I.; Aparicio, F. J.; Borrás, A.; Barranco, A.; Álvarez-Herrero, A.; Fernández-Rodríguez, M.; González-Elipe, A. R. *The Journal of Physical Chemistry C* **2009**, *113*, 431.
- (12) *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press Inc.: San Diego (US), 1990.
- (13) Yasuda, H. K. *Luminous Chemical Vapor Deposition and Interface Engineering*; Marcel Dekker: New York, 2004.
- (14) Denes, F. S.; Manolache, S. *Progress in Polymer Science* **2004**, *29*, 815.
- (15) Barranco, A.; Biemann, M.; Widmer, R.; Groening, P. A. *Advanced Engineering Materials* **2005**, *7*, 396.
- (16) Barranco, A.; Aparicio, F.; Yanguas-Gil, A.; Groening, P.; Cotrino, J.; González-Elipe, A. R. *Chemical Vapor Deposition* **2007**, *13*, 319.
- (17) Aparicio, F. J.; Borrás, A.; Blaszczyk-Lezak, I.; Gröning, P.; Álvarez-Herrero, A.; Fernández-Rodríguez, M.; González-Elipe, A. R.; Barranco, A. *Plasma Processes and Polymers* **2009**, *6*, 17.
- (18) Aparicio, F. J.; Holgado, M.; Borrás, A.; Blaszczyk-Lezak, I.; Griol, A.; Barrios, C. A.; Casquel, R.; Sanza, F. J.; Sohlström, H.; Antelius, M.; González-Elipe, A. R.; Barranco, A. *Advanced Materials* **2011**, *23*, 761.
- (19) Barranco, A.; Groening, P. *Langmuir* **2006**, *22*, 6719.
- (20) Aparicio, F. J.; Lozano, G.; Blaszczyk-Lezak, I.; Barranco, A. n.; Míguez, H. n. *Chemistry of Materials* **2010**, *22*, 379.
- (21) Sanchez, C.; Lebeau, B.; Chaput, F.; Boilot, J. P. *Advanced Materials* **2003**, *15*, 1969.
- (22) Barranco, A.; Cotrino, J.; Yubero, F.; Girardeau, T.; Camelio, S.; González-Elipe, A. R. *Surface and Coatings Technology* **2004**, *180-181*, 244.
- (23) Long, G. L.; Winefordner, J. D. *Analytical Chemistry* **1983**, *55*, 712A.

- (24) NIST Chemistry WebBook database. In *August 2011*; <http://webbook.nist.gov/chemistry>.
- (25) Zeze, D. A.; Silva, S. R. P.; Brown, N. M. D.; Joyce, A. M.; Anderson, C. A. *Journal of Applied Physics* **2002**, *91*, 1819.
- (26) Sokrates, G. *Infrared Characteristic Group Frequencies: Tables and Charts*; Wiley-Interscience: New York, 1994.
- (27) Tanaka, K.; Nishio, S.; Matsuura, Y.; Yamabe, T. *Journal of Applied Physics* **1993**, *73*, 5017.
- (28) Bisticic, L.; Baranovic, G.; Mlinaric-Majerski, K. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **1995**, *51*, 1643.
- (29) Jensen, J. O. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2004**, *60*, 1895.
- (30) Shirafuji, T.; Nishimura, Y.; Tachibana, K.; Ishii, H. *Thin Solid Films* **2009**, *518*, 993.
- (31) *Plasma Polymer Films*; H. Biederman, Ed; Imperial College Press: London, 2004.
- (32) Grill, A. *Cold Plasma in Materials Fabrication*; IEEE Press: Birmingham (GB), 1994.
- (33) Peri, S. R.; Kim, H.; Akgun, B.; Enlow, J.; Jiang, H.; Bunning, T. J.; Li, X.; Foster, M. D. *Polymer* **2010**, *51*, 3971.
- (34) Barranco, A.; Cotrino, J.; Yubero, F.; Espinós, J. P.; Benítez, J.; Clerc, C.; González-Elipe, A. R. *Thin Solid Films* **2001**, *401*, 150.
- (35) Katoh, R.; Sinha, S.; Murata, S.; Tachiya, M. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, *145*, 23.
- (36) Nijegorodov, N.; Mabbs, R.; Downey, W. S. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2001**, *57*, 2673.
- (37) Lakowicz, J. R.. *Principles of Fluorescence Spectroscopy*; Springer: Berlin, 1999.
- (38) Kim, M.C.; Cho S.H.; Han, J.G.; Hong, B.Y.; Kim, Y.J.; Yang, S.H.; Boo J.-H.; *Surface and Coatings Technology* **2003**, 169-170, 595.
- (39) Goktas, H.; Ince, F.G.; Iscan, A.; Yildiz, I.; Kurt, M.; Kaya, I.; *Synthetic Metals* **2009**, *159*, 2001.
- (40) Saravanan, S.; Anantharaman, M.R.; Venkatachalam, S.; D.K., Avasthi; *Vacuum* **2008**, *82*, 56.
- (41) Johnson, P. C.; Offen, H. W. *Chemical Physics Letters* **1973**, *18*, 258.
- (42) Vitukhnovsky, A. G.; Sluch, M. I.; Warren, J. G.; Petty, M. C. *Chemical Physics Letters* **1991**, *184*, 235.
- (43) Seko, T.; Ogura, K.; Kawakami, Y.; Sugino, H.; Toyotama, H.; Tanaka, J. *Chemical Physics Letters* **1998**, *291*, 438.
- (44) Martinu, L.; Poitras, D. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2000**, *18*, 2619.
- (45) Shi, F. F. *Surface and Coatings Technology* **1996**, *82*, 1.
- (46) Enlow, J. O.; Jiang, H.; Grant, J. T.; Eyink, K.; Su, W.; Bunning, T. J. *Polymer* **2008**, *49*, 4042.
- (47) Jiang, H.; O'Neill, K.; Grant, J. T.; Tullis, S.; Eyink, K.; Johnson, W. E.; Fleitz, P.; Bunning, T. J. *Chemistry of Materials* **2004**, *16*, 1292.
- (48) Dislich, H. *Angewandte Chemie International Edition in English* **1979**, *18*, 49.
- (49) Paquet, C.; Cyr, P. W.; Kumacheva, E.; Manners, I. *Chemistry of Materials* **2004**, *16*, 5205.
- (50) Han, X.; Naeher, L. P. *Environment International* **2006**, *32*, 106.

Table 1. Summary of the remote plasma deposited PA thin films (~150 nm) grown using different deposition protocols as indicated and the corresponding thin film absorbance at 440 nm after background correction.

Sample	^a r _p /r _a	Absorbance at 440 nm
^b PA-3	3	0.134
PA-1.5	1.5	0.066
PA-1	1	0.040
PA-0.5	0.5	0.032

^aRatio between deposition rates associated to perylene (r_p) and adamantane (r_a) supplies.

^bFor this preparation perylene deposition was not interrupted by the shutter

FIGURE CAPTIONS

Figure 1. ToF-SIMS spectra of (a) perylene (RPD-P), (b) adamantane (RPD-A) and (c) perylene-adamantane (PA-3) remote plasma deposited thin films. The spectral regions corresponding to adamantane and perylene molecular ions are shown in an enlarged scale in (c) and (d), respectively.

Figure 2. FTIR spectra of perylene-adamantane remote plasma deposited films PA-1 and PA-3 in comparison with the spectra of perylene (RPD-P) and adamantane (RPD-A) remote plasma deposited films and the corresponding sublimated layers.

Figure 3. Surface topography of perylene-adamantane remote plasma deposited films. AFM images (a, b) and the corresponding linear profiles (c, d) of plasma deposited films PA-3 (a, c) and PA-1.0 (b, d).

Figure 4. UV-Vis spectra of a set of perylene-adamantane remote plasma deposited thin films (~150 nm) prepared with different concentrations of perylene (see Table 1). The spectra of pure adamantane (RPD-A) and perylene (RPD-P) remote plasma deposited thin films and of a sublimated layer of perylene are included for comparison.

Figure 5. (a) Fluorescence spectra of a set of perylene-adamantane remote plasma deposited films prepared with different concentrations of perylene (see Table 1). Fluorescence spectrum of a 10^{-6} M solution of perylene in toluene is included for comparison. (b) Fluorescence spectra of a 10^{-6} M solution of perylene in toluene, a sublimated layer of perylene and of two remote plasma deposited films of RPD-P and PA.

Figure 6. (a) Refractive index curves determined by VASE for a set of perylene-adamantane (PA) remote plasma deposited films prepared with different concentrations of perylene (see Table 1) and for adamantane (RPD-A) and perylene (RPD-P) remote plasma deposited films.

Figure 7. (a) Evolution of the emission spectra of a perylene-adamantane remote plasma thin film PA-1.5F deposited on frosted fused silica when it is exposed to a 5 ppm NO_2 /air flow during 16 h at room temperature. The spectra were collected at intervals of 1h. Arrow indicates the time evolution. (b) Evolution of fluorescence intensity at $\lambda = 507$ nm of different perylene-adamantane plasma deposited films as function of the exposure time to NO_2 /air flow of 5 ppm. Samples PA-3 and PA-1.5 were deposited on polished fused silica and sample PA-1.5F on frosted fused silica. (c) Evolution of fluorescence intensity at $\lambda = 507$ nm for sample PA-1F exposed to 0.5 ppm of NO_2 in air.

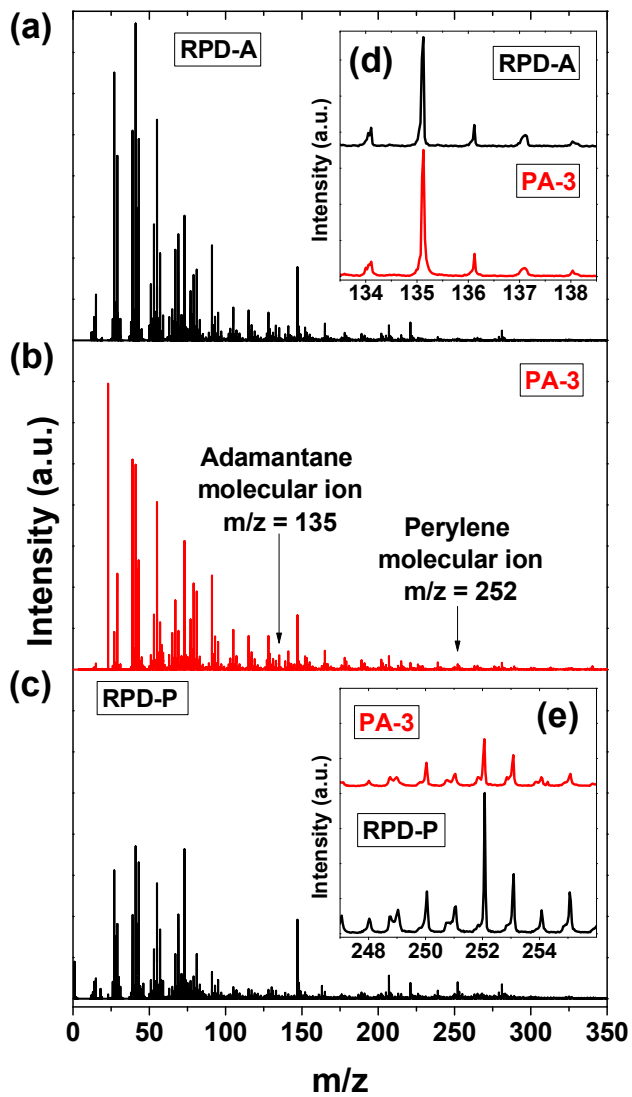


Figure 1

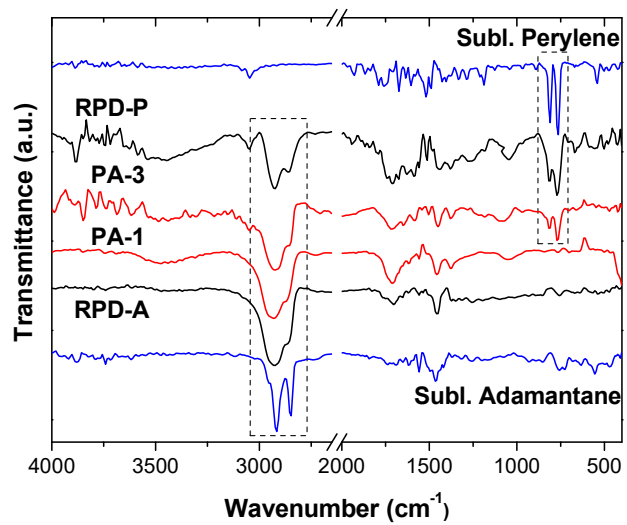


Figure 2

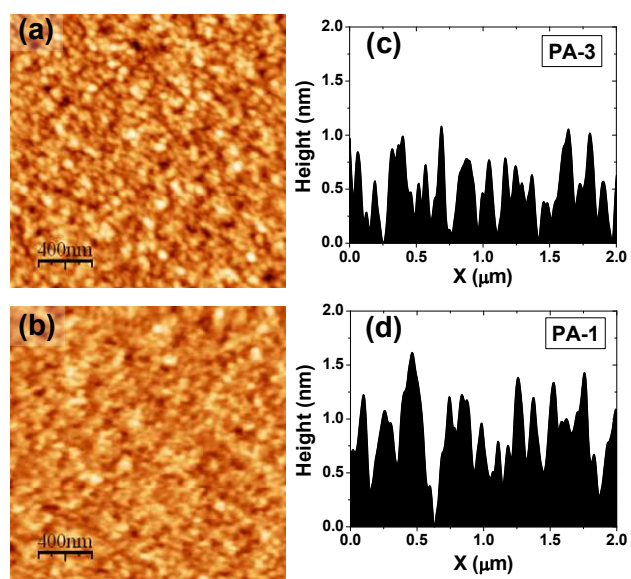


Figure 3.

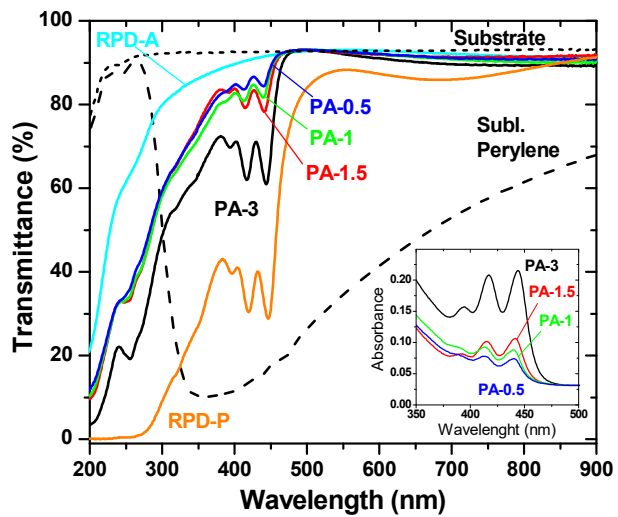


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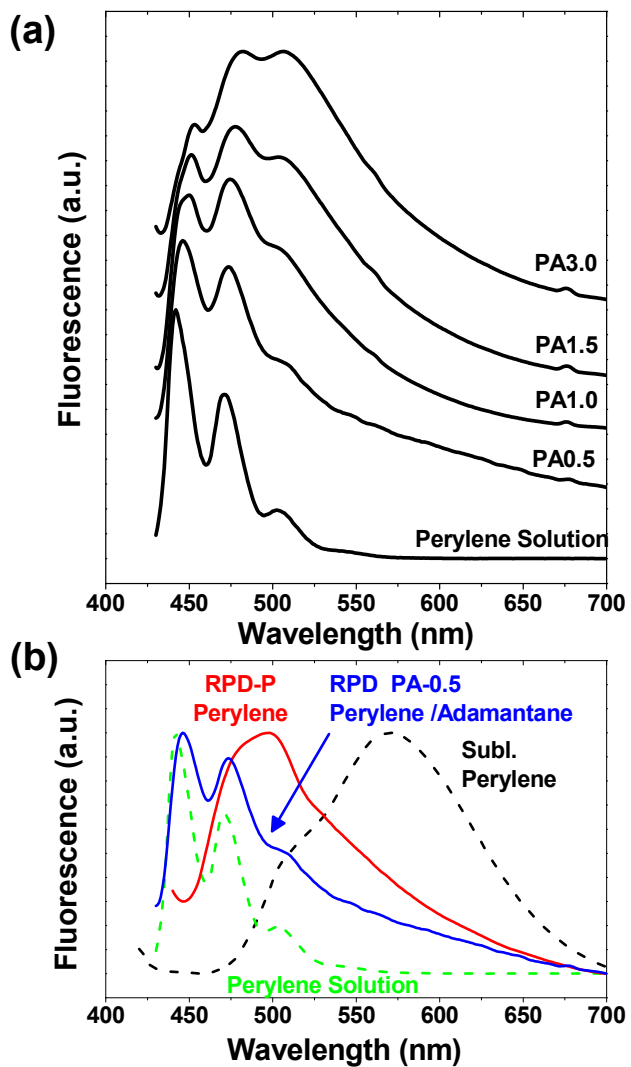


Figure 5.

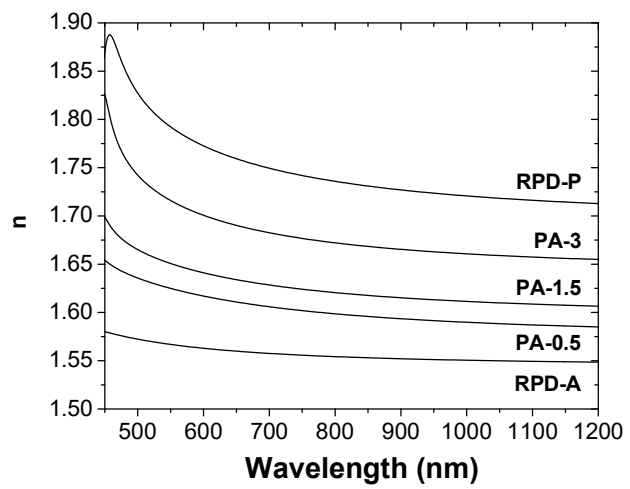


Figure 6

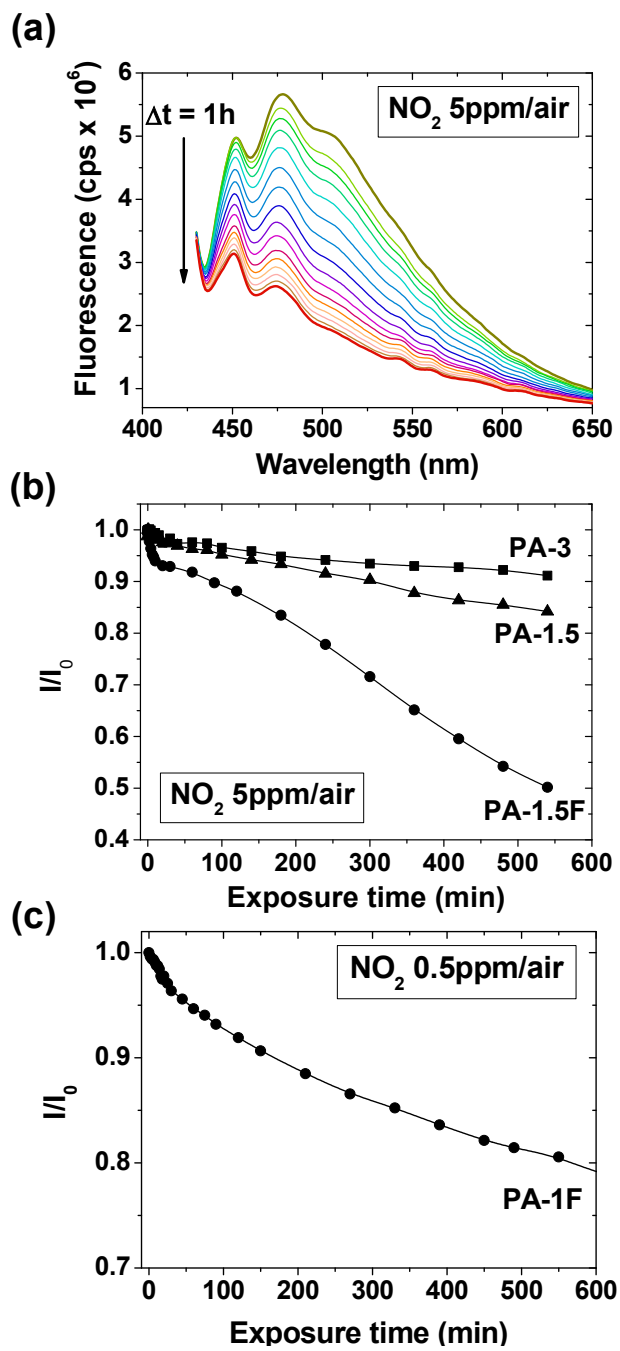


Figure 7.

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