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# Stabilization of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine thin film morphology with UV light

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## Abstract

Owing to their low glass transition temperature,  $T_g$ , amorphous thin films of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD) undergo morphological changes even at room temperature. It has been noticed previously that exposure to UV light can increase apparent  $T_g$  of TPD films and thus stabilize their morphology. However, the reason behind increase in structural stability was not examined at the time. Here we present evidence that TPD molecules undergo photo-oxidation in air when exposed to  $\lambda \approx 350$  nm radiation and that less than 5% of the photo-oxidized species are needed to prevent dewetting of thin TPD films. We propose that photo-oxidized TPD species bind strongly to both ordinary TPD molecules and to terminal hydroxyl groups at the substrate surface, which decreases mobility of TPD molecules and makes thin TPD film less prone to morphology changes.

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## Introduction

There is a growing interest in organic electronic devices, primarily in organic light emitting diodes, thin film transistors, and organic photovoltaics [1,2]. Typically, these devices have layered structure, in a form of thin amorphous films of different functional materials [3]. Amorphous films often have an advantage over polycrystalline, due to easy and reproducible deposition and spatial homogeneity of optical and transport properties [4]. Organic thin films are usually obtained either by spin-coating or by physical vapor deposition. Both processes lead to thermodynamically unstable amorphous films that are prone to various types of structural degradation. These include changes in thin film morphology, which may occur at considerably lower temperatures in comparison to the bulk  $T_g$  [5]. To optimize the performance of organic electronic devices one has to balance optoelectronic properties with morphological properties of materials.

In this work, we focus on increase of the structural stability of amorphous thin films of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD) using UV radiation. TPD is a well-known hole-transport material frequently used in organic optoelectronic devices [6,7]. The  $T_g$  of TPD bulk is 60°C [5] but for films thinner than 40 nm dewetting occurs even at room temperature if deposited on indium-tin oxide (ITO) or a fused-silica substrate [8]. In such films the energy of non-covalent interactions is comparable to the energy of thermal fluctuations and thus can lead to morphological and structural changes driven by minimization of Gibbs free energy.

Following a brief report on increased stability of UV irradiated TPD films [9], we investigated the underlying mechanism responsible for this phenomenon. Changes on the molecular level of amorphous TPD thin films were studied using proton nuclear magnetic resonance ( $^1\text{H}$  NMR) and mass spectrometry, while changes in morphology were tracked by optical microscopy.

### 1. Experimental details

Amorphous thin films of TPD (Sigma Aldrich, 99% purity) were evaporated in high-vacuum with  $2 \times 10^{-4}$  Pa of background pressure, using a tantalum Knudsen effusion cells with 3 mm pinhole. The temperature of evaporator was kept at 190°C powered by Sorensen DCS8-125E regulated by an active feedback loop. Films were deposited on rectangular (25mm x 75mm) substrates such as ITO, fused silica, and a boron-silicate glass. Prior to deposition, the substrates were cleaned with a detergent soap, sonicated in isopropanol and then in ultrapure water (18.2 MΩcm at 25°C) prepared using a Milli-Q ultrafiltration system (Millipore) and dried in a nitrogen flow.

One end of the rectangular substrate was positioned 30 mm above the evaporator pin-hole, yielding thin films with a cosine-like thickness profile gradient [8]. As a result, in a single deposition one can obtain various film thicknesses, changing gradually for an order of magnitude between the two ends of the substrate. The typical deposition lasted for 10 minutes, with the evaporator held at 190 °C, which produced thin films with about 70 nm thickness at the maxima. The thickness  $d$  was determined from absorption measurements using a single beam Beckman Coulter DU 700 spectrophotometer and the value of TPD absorption coefficient  $1.6 \times 10^5 \text{ cm}^{-1}$  at 355 nm [10]. The shape of the thickness profile was determined by measuring the intensity of the UV light transmitted through a 2 mm hole positioned in front of a movable substrate.

The films were irradiated in air and in high-vacuum ( $2 \times 10^{-4}$  Pa) with the exposure times ranging from 1 to 10 hours. A Hg lamp, which delivered about  $1.7 \text{ mWcm}^{-2}$  in the 300-400 nm range (as determined by a Solar Light Co. PMA 2110 UVA sensor) was used as a source of UV light. Only one half of the film was exposed to UV light along the thickness profile gradient for comparison purposes, so the effects of radiation on the film morphology could be assessed for every film thickness.

Mass spectra of TPD films dissolved in toluene were recorded using a Waters GCT premier time-of-flight mass spectrometer equipped with ionization/field desorption ion sources. Chemical changes upon irradiation were deduced from  $^1\text{H}$  NMR spectra obtained with a Varian 400 MHz spectrometer. The NMR spectra were

recorded at room temperature after dissolving TPD films in deuterated chloroform. Dewetting dynamics of TPD films was recorded by a CCD camera (Sanyo VCC-3700P with 500 x 582 pixels) mounted on an inverted microscope (IX71 Olympus) using a 20X magnification in a phase contrast mode.

## 2. Results and discussion

As-deposited amorphous films of TPD appear uniform with smooth surface independent of the film thickness. Within a few hours after deposition, dewetting of TPD film begins by formation of holes in the film, with a bare substrate exposed at the hole bottom. As shown by Suljovrujic et al. [8], such perforated film gives rise to different morphology features at different film thicknesses. These morphologies range from isolated droplets at the thin end of the film to volcano-like features found near the critical film thickness where dewetting process stops (see below). For intermediate film thicknesses dewetting leads to a network of interconnected droplets, which is captured by a CCD camera attached to a microscope (see Fig. 1). The dewetting process in TPD appears very similar to dewetting of polystyrene thin films on SiO<sub>2</sub> substrate [11], which is considered as a model system for dewetting phenomena in ultrathin films. For this system, there is an excellent agreement between theory and experiment (see a review article of R. Blossey [11]), which applies not only to morphology details but also to dynamics of the dewetting process.

The rupture of TPD film at  $d \approx 30$  nm can be noticed a couple of hours after the deposition. It is conceivable that dewetting of TPD films starts immediately after the deposition but it takes some time before such changes become visible by an optical microscope. The number of the holes per unit area grows steadily during the next 24 hours but some small sections of the film still remain intact. As the dewetting process continues, adjacent holes coalesce, creating a labyrinth of TPD segments (white stripes) on a fused-silica substrate (the black background). The dewetting process at this film thickness is finished after 36 hours when

no further changes in TPD morphology are noticeable. While there is a great similarity with the morphology of polystyrene, the dynamics of TPD is an order of magnitude slower.

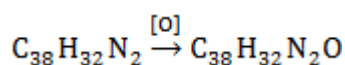
Dewetting of TPD films on fused silica halts at some critical film thickness, which depends on the ambient temperature and is found at  $d_c = 38$  nm for 21°C. As shown in Fig. 2, the dewetted section of the film looks as frosted glass, which is a consequence of Mie scattering from TPD particles of the sizes comparable to the wavelengths of visible light. A sharp line separating dewetted section from smooth part of the film follows constant film thicknesses while its curvature reflects axial symmetry of the film deposited from a pin-hole. Similar values for critical film thicknesses were found on boron-silicate glass and ITO coated substrates, which confirms that the already low  $T_g$  of bulk TPD is further lowered in thin films deposited on hydrophilic substrates. Such an ephemeral morphology is the main reason that TPD has been replaced in organic optoelectronic devices by other hole-transport materials with considerably higher  $T_g$  values [4,12].

Recently, a couple of brief reports have suggested that spontaneous morphological changes in thin TPD films of the kind described above can be suppressed by exposing them to UV light after the deposition [9,13]. Indeed, as shown in Fig. 2b, one half of the film, exposed to UV light for 2 hours in air, remained smooth and transparent at room temperature while the other half dewetted in the way already described. No sign of dewetting was found for illuminated films even if subjected to temperatures as high as 90°C. This is significantly higher than the  $T_g$  of TPD bulk, which may be of importance for technological applications. We note that UV radiation does not stabilize morphology of TPD thin films if irradiated in vacuum after the deposition under otherwise same experimental conditions.

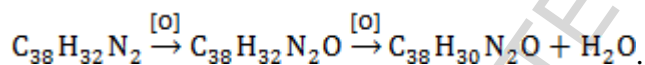
It is well-known that all three substrates used in this study (boron-silicate glass, fused silica, and ITO) are hydrophilic to some extent, which explains why spontaneous dewetting of (hydrophobic) TPD films occurs on all three surfaces. Important finding here is that stabilization of TPD morphology with UV light is surface independent. TPD is one of the best organic hole-transport materials whose application is hampered by its

fragile morphology. The discovery that morphology of TPD films on ITO substrate can be stabilized by UV light [9] may solve this problem provided that TPD transport properties are not affected by it. We intend to address this important question in our future studies.

We propose that more stable morphology of UV-exposed TPD films is linked to photo-oxidation processes for which direct evidence was derived from mass spectroscopy measurements. The mass spectrum of pristine TPD film has only one peak at 516 a.u., while UV-exposed TPD sample reveals two additional peaks at 530 a.u. and 532 a.u., as shown in Fig. 3. The main peak is due to TPD molecule,  $C_{38}H_{32}N_2$ , while the two additional peaks belong to photo-oxidized TPD species with molecular formulas  $C_{38}H_{30}N_2O$  and  $C_{38}H_{32}N_2O$ . It is likely that these arise through oxidation processes of the kind:



and



The UV-exposed TPD films could give rise to oligomers of photo-oxidized TPD species too, but no evidence for this was found in experiment. We note that mass of TPD dimers falls into detection window of our instrument but heavier TPD oligomers do not. Assuming no oligomers were formed, from relative intensities of relevant peaks in Fig. 3 it appears that only a small fraction of TPD species have been photo-oxidized in our experiment. From the mass spectroscopy data it remains unclear if there were more than one photo-oxidized TPD species for each of the two masses detected and which part of the molecule was oxidized. We tried to shed some light on those questions from NMR data presented below.

Proton NMR spectra of TPD thin films before and after exposure to UV irradiation are shown in Fig. 4. Aided by calculated proton NMR spectra of TPD molecule [14] and the known chemical shifts of various molecular fragments/groups [15], we were able to assign all of the observed resonances of pristine TPD film. The resonance at 2.3 ppm belongs to protons (1) from two methyl groups while a large number of resonances

centered at 7 ppm belong to protons (2-7) from phenyl rings. The smaller ppm values of the chemical shift the larger electron density around the proton is; hence it is plausible that the methyl group is the most susceptible to oxidation. Such an outcome would produce a new set of resonances from protons of  $-H_2COH$  group but also would cause a small downfield shift of the proton resonances associated with phenyl rings. This is a consequence of so-called induction effect, which manifests through a shift in the local electron density due to introduction of a distant atom of different electron affinity.

The trends observed in  $^1H$  NMR spectrum of UV irradiated TPD sample in Fig. 4b are in qualitative agreement with above expectations. The resonances of pristine TPD sample are still dominant but a number of additional weak resonances of photo-oxidized TPD species are clearly visible. Unfortunately, most of them are buried under intense TPD resonances thus making their assignment impossible. We can speculate that the resonances between 4.5 ppm and 5.5 ppm belong to protons from  $-H_2COH$  group, in analogy with  $^1H$  NMR spectrum of phenylmethanol [15], where these resonances are found at 4.58 ppm. The group of additional dense resonances at around 7.6 ppm should be ascribed to protons from phenyl rings of photo-oxidized TPD species. These resonances are shifted downfield for up to 0.2 ppm from the resonances of TPD protons with smallest electron density (3). In addition, there are some weak resonances at 7.9 ppm and 8.4 ppm which should also belong to the protons from phenyl rings. It is unlikely that distant  $-H_2COH$  group can cause such a large downfield shift, hence we suppose that phenyl rings of TPD are also susceptible to photo-oxidation. Whether we have one or more different species of that kind remains an open question.

Like the previous studies [13,16,17], our study shows that both absorption and photoluminescence spectra of air-exposed TPD films are affected by UV radiation. As can be seen in Fig. 3, exposure of TPD to UV light leads to a slow and steady (1% per hour) decrease in the intensity of absorption bands in 325 – 400 nm region and much faster decrease in photoluminescence intensity. We found no observable changes in the absorption and luminescence spectra of the films irradiated in vacuum, consistent with the proposed photo-oxidation phenomena. Low et al. [18] showed that the TPD oxidation causes large spectral shifts of the



absorption bands out of near UV region. Hence one can correlate a decrease in absorption intensity with the extent of TPD oxidation, which was found to be a small fraction of TPD film in agreement with  $^1\text{H}$  NMR and mass spectrometry data.

Photoluminescence spectrum (Fig. 5) of UV-exposed TPD films fades away much more rapidly than the absorption and thus it cannot be attributed to depletion of TPD molecules due to photo-oxidation. Instead, we propose that energy transfer between photo-excited TPD molecules and photo-oxidized TPD species quenches TPD luminescence. From the energy transfer studies in thin organic films is known that only a few percent of acceptor species can completely quench donor luminescence [19]. For this to happen, acceptor species need to be distributed randomly throughout entire film. We believe this is the case with our photo-oxidized TPD species since our films were sufficiently thin to assure negligible change of UV light intensity with the depth and for the fact that oxygen diffuses easily into unprotected amorphous films [20].

A random distribution of photo-oxidized TPD species is also required to explain more stable morphology of UV-exposed TPD films. TPD is nearly non-polar hydrophobic molecule [21] whose interaction with the glass or ITO substrate is weaker than van der Waals interaction with its own species. This is the main reason why thin TPD films on polar substrates have lower  $T_g$  than in the bulk. The photo-oxidized TPD molecules are likely to have a polar character. Such species can interact strongly with terminal OH groups from the substrate, which will stabilize film in respect to dewetting. One can also expect that the presence of dipole-dipole and dipole-induced-dipole interactions between different species in the film will further increase its thermal stability. The studies are underway to determine a precise relationship between degree of oxidation and  $T_g$  of the film for various film thicknesses.

### 3. Conclusion

We investigated the mechanism that leads to increase of thermal stability of amorphous thin TPD films illuminated by UV light. Irradiated films are stable up to at least 90°C, which is a temperature significantly higher than  $T_g$  of TPD. Dewetting process is suppressed in exposed films, as one can evidence by a naked eye. Inspection on the molecular level by means of time-of-flight mass spectrometry technique and  $^1\text{H}$  NMR indicates that UV light leads to photo-oxidation of TPD molecules. Absorption bands at 315 and 355 nm and photoluminescence decrease upon irradiation. However, the rate of decrease of photoluminescence is much faster, possibly as a consequence of luminescence quenching by the energy transfer between photo-excited TPD and photo-oxidized TPD species. We propose that photo-oxidized TPD molecules have an increased dipole moment compared to TPD and that the dipole-dipole interactions of new species with OH groups from the substrate and molecules in a film increase its thermal stability.

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## Figure captions

Fig. 1: Dewetting dynamics of  $\sim 30$  nm thick TPD film (shown in gray). It begins with random formation of holes (the black spots) followed by their coalescence and formation of TPD stripes (white areas) on the fused silica substrate (black background). The gray scale (black to white) reflects relative height of the objects.

Fig. 2: The thickness profile as a function of the distance  $r$  from the maximum of TPD film across 7.5 cm long fused silica substrate, which is spatially aligned with the photograph a) of the film after dewetting. Shown in b) is a photograph of another TPD film of a nearly identical thickness profile whose upper half was exposed for 2 hours to UV radiation during dewetting.

Fig. 3: Mass spectrum of TPD film exposed to UV light. Besides the ones of TPD molecule, we observe tiny peaks at 530.2 and 532.2 a.u. Note that each of these peaks is accompanied with two satellite peaks due to isotope species whose relative intensities are in quantitative agreement with theoretical predictions.

Fig. 4: a)  $^1\text{H}$  NMR spectrum of a dissolved pristine TPD film with the main resonance assigned to protons attached to 10 unique carbon atoms in TPD; see the drawing of TPD molecular structure shown in the inset. b) The corresponding spectrum of UV irradiated TPD film with additional resonances (indicated by arrows and circles) due to photo-oxidized TPD species.

Fig. 5: Change in intensity of absorption and photoluminescence spectra of 115 nm thick TPD film during the exposure to UV light.

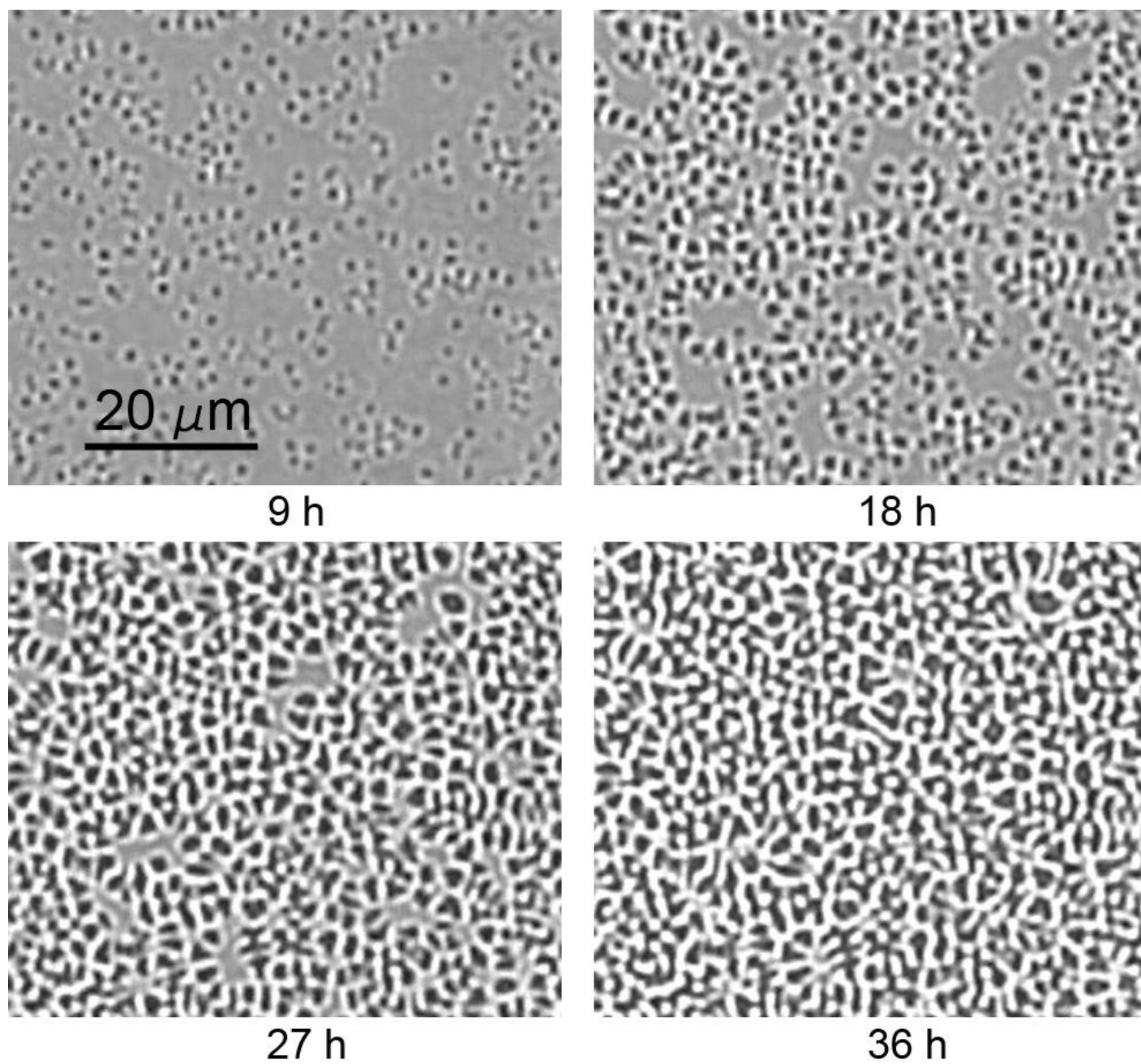


Figure1

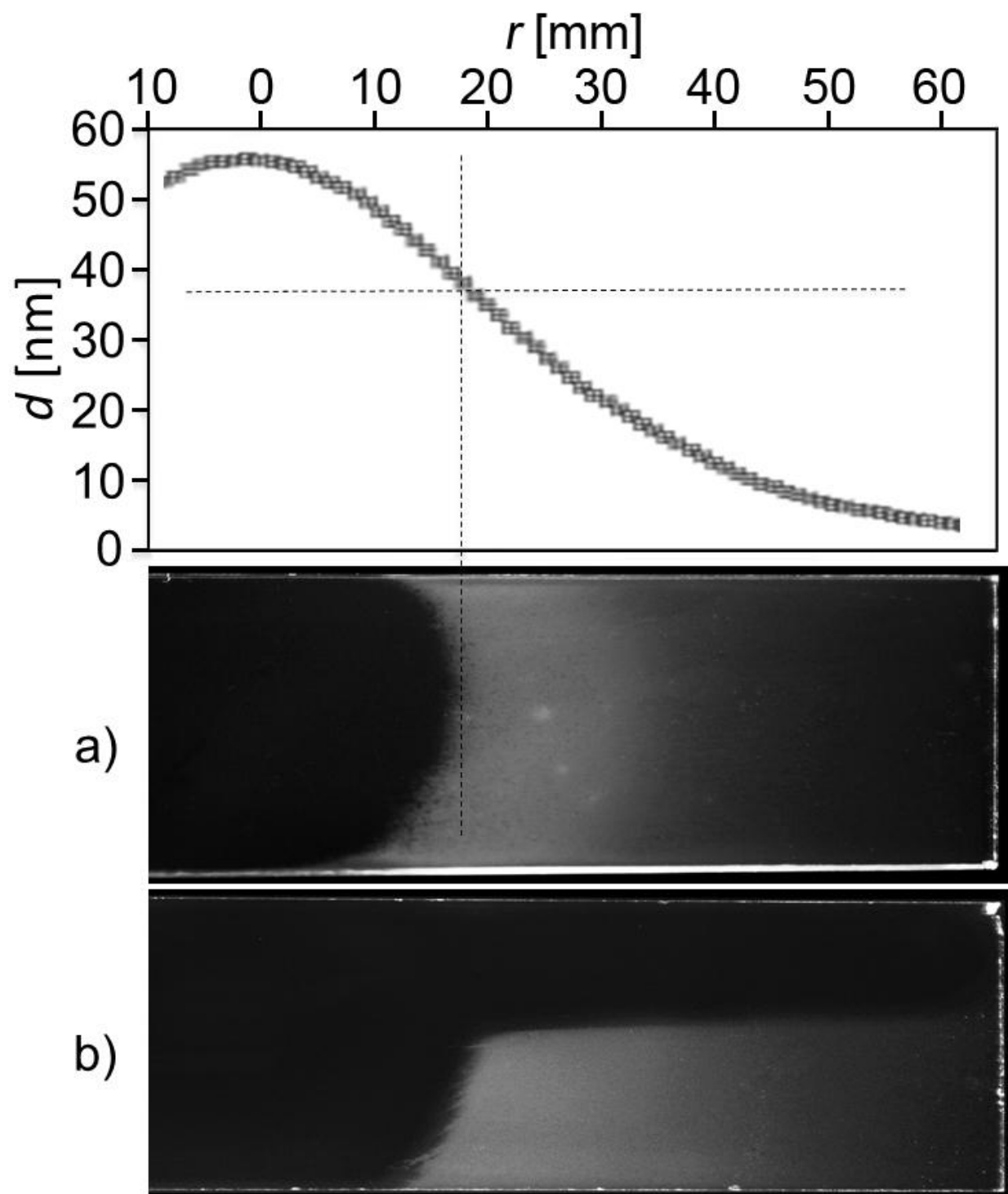


Figure2

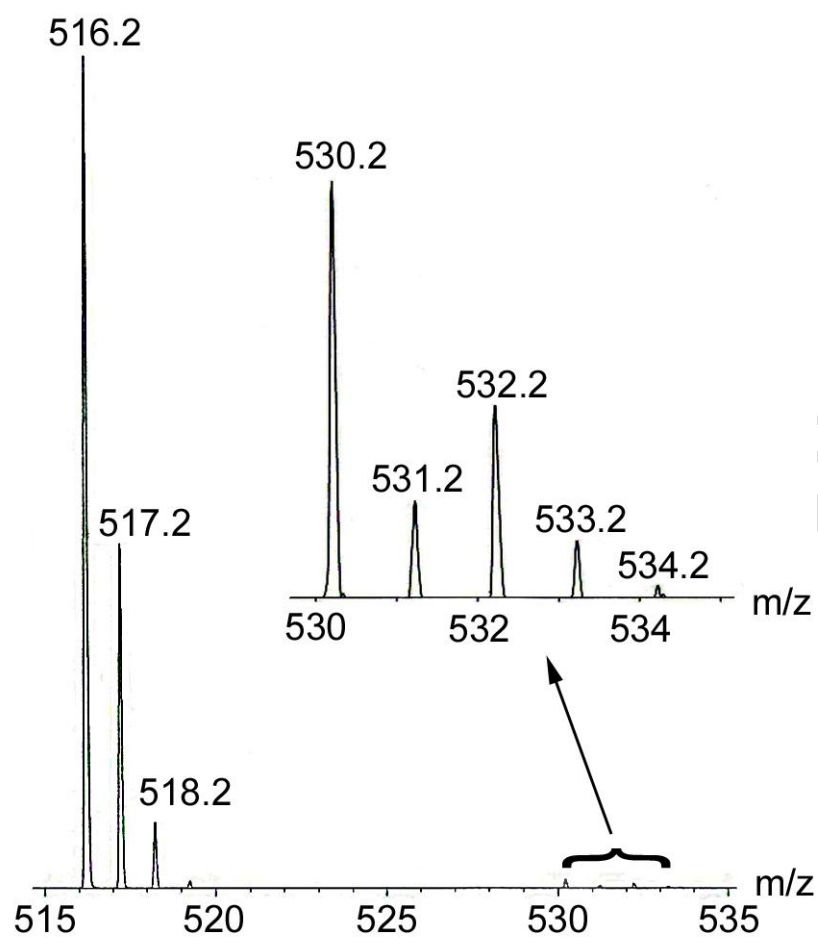


Figure3



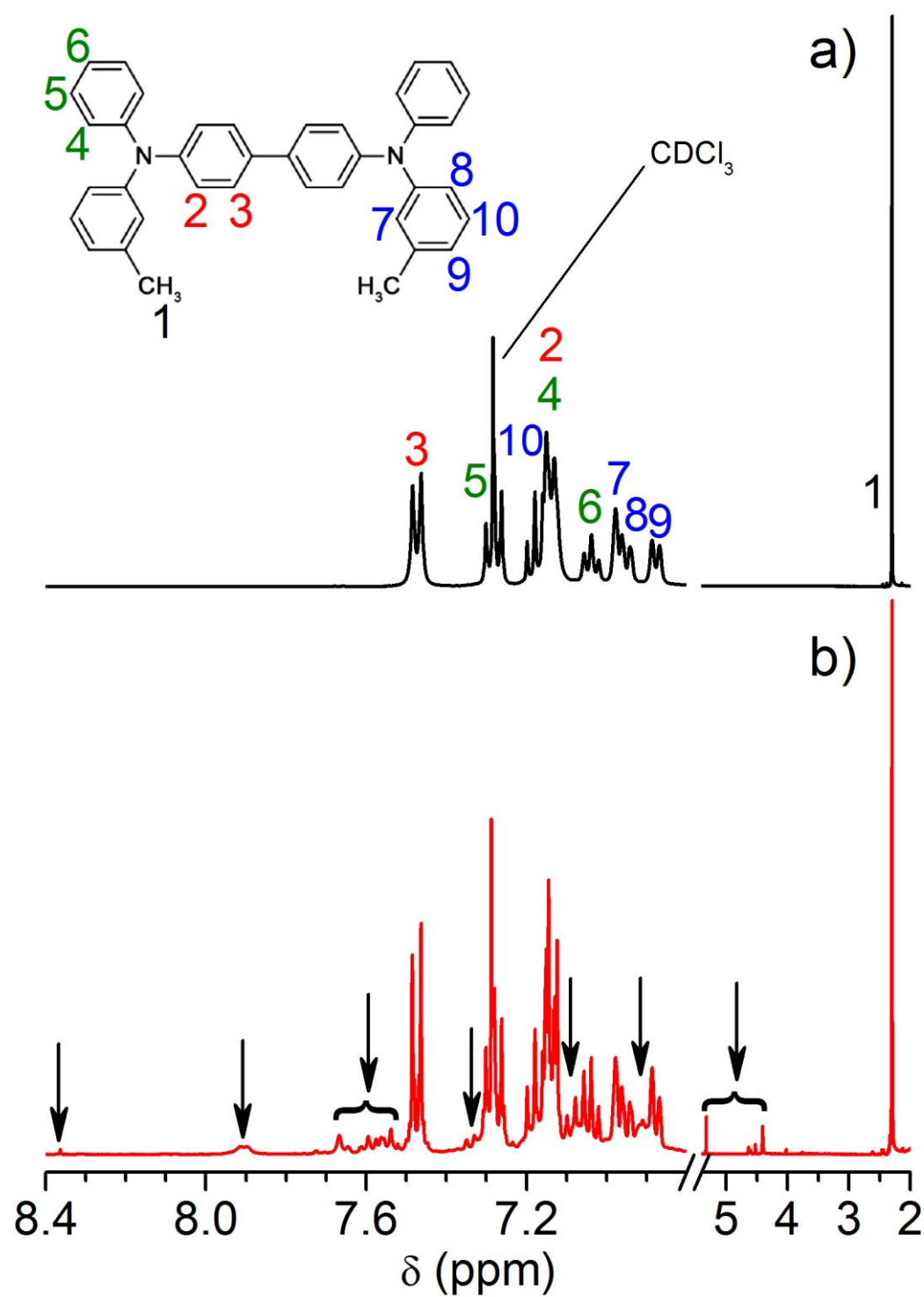
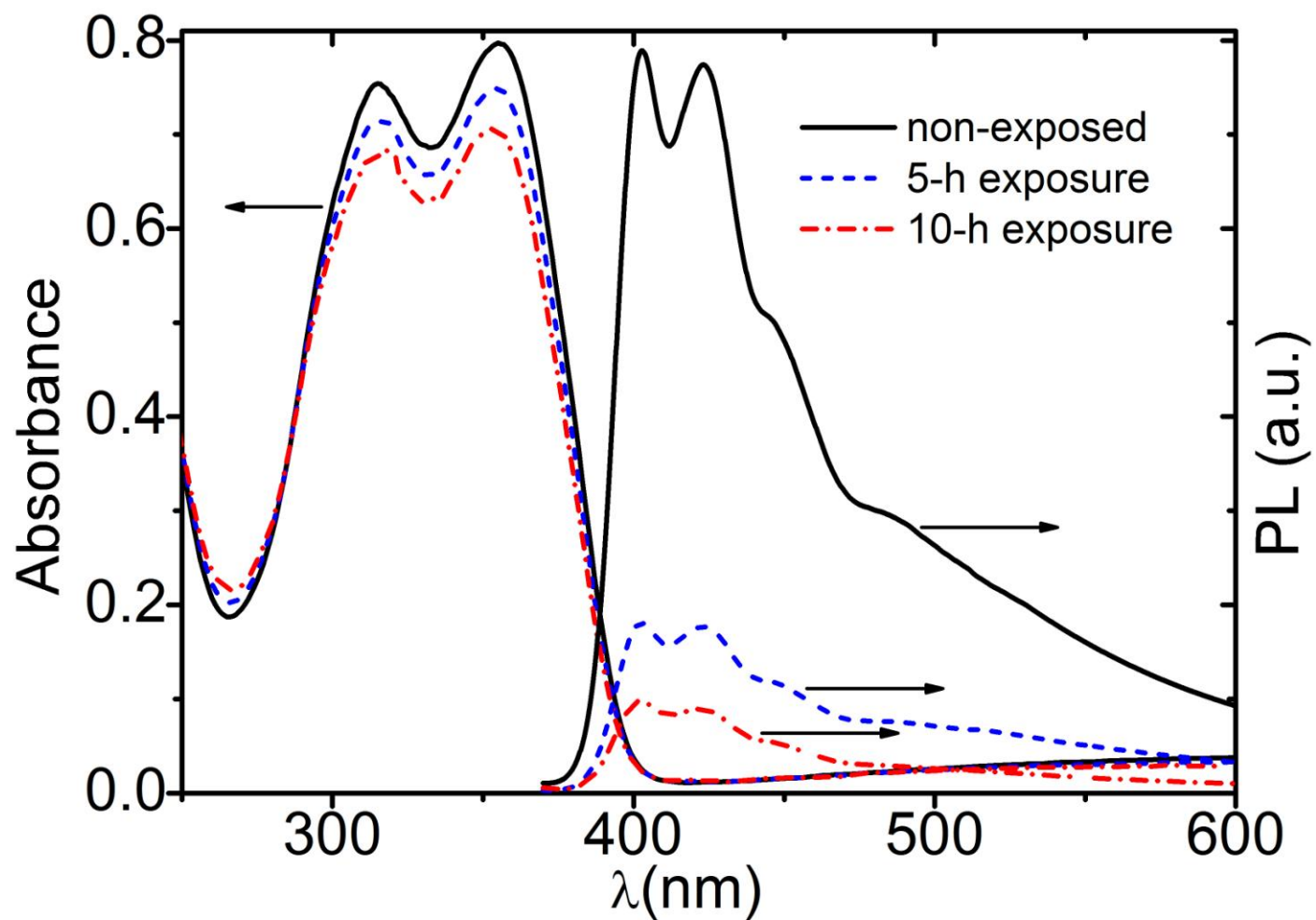


figure4



• Figure5

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- We made variable thickness TPD films and exposed them to UV light under ambient conditions.
- Mass spectroscopy and proton NMR measurements of irradiated and pristine TPD films.
- TPD molecules undergo oxidation process under UV light irradiation.
- Dipole-dipole interactions may be responsible for stabilization of morphological changes.