# Exciplex Formation and Energy Transfer in Mixed Films of Phthalocyanine and Perylene Tetracarboxylic Diimide Derivatives

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The absorption and emission properties of co-evaporated and bilayer phthalocyanine−perylene tetracarboxylic diimide (PTCD) thin films have been examined in search for new emitters. The identification of exciplex emission in co-evaporated thin solid films of *N*,*N*'-bis(neopentyl)-3,4,9,10-perylenebis(dicarboximide) (BNPTCD) and titanyl(IV) phthalocyanine (TiOPc) is reported for the first time. The efficiency of the exciplex emission is correlated with a high degree of mixing in the co-evaporated mixed film. The homogeneity of the emission from the surface of the mixed film is visualized using the global imaging technique. The chemical detection of the mixing in the film is visualized using Raman global imaging. The fact that exciplex formation is not a common occurrence when mixing these materials is illustrated with the emission properties of co-evaporated mixed chloroindiumphthalocyanine (ClInPc)−BNPTCD films. In ClInPc−BNPTCD mixed films there is no exciplex emission and in turn energy transfer is the main pathway for internal relaxation. For comparison, bilayer films of BNPTCD/Pc were fabricated and studied as model systems of two separated phases with a single interface. The effect of thermal annealing on film structure, molecular organization, and phase separation in the mixed films was investigated using transmission and reflection−absorption (RAIRS) infrared spectroscopy. The infrared data and AFM topographical images provide information that allows one to correlate film structure with the observed emission properties.

## Introduction

The formation of excited van der Waals dimers, by aromatic molecules, giving rise to excimer or exciplex emissions, has been investigated using several techniques[1] including supersonic jet experiments.[2] The emission properties of co-deposited and dye-doped organic thin films have been successfully used in the development of practical organic lasers.[3−5] These systems usually exhibit Förster-type energy transfer,[1,6] which significantly increases the laser efficiency. Polymer blending and molecular mixing seem to be the most promising way to obtain blue and white emission in organic electroluminescent devices.[7,8] Just by the interposing of a mixed co-deposited layer,[9] or simple doping,[10] the performance of light-emitting diodes can be highly improved. In organic emitting devices the formation of exciplexes appears to play an important role in the photoluminescent (PL) and electroluminescent (EL) characteristics of bilayer polymeric and molecular thin films.[8,11−14] An exciplex is formed by two distinct monomers that are only bound in an excited electronic state. Exciplex emission has been used in EL thin film devices to tune the emission color or to broaden the spectral width to achieve near-white emission. The literature concerning the study of exciplex formation in blended polymeric or molecular-doped polymeric sys-

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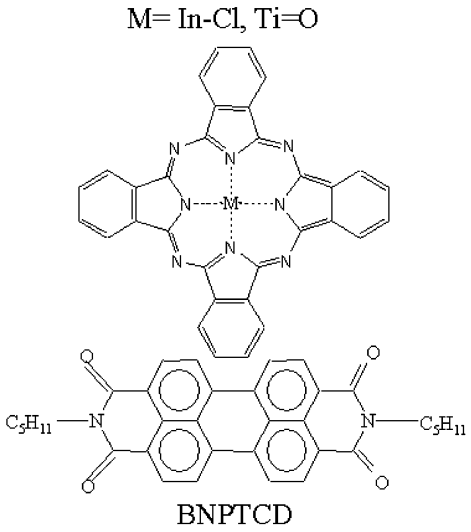
tems is extensive.[7,11,12,15,16] However, little has been reported on the properties of mixed films fabricated with small molecular weight organic materials where exciplex formation may take place.[13,17,18]

Phthalocyanines (Pcs) and perylene tetracarboxylic diimides are well-known organic materials, which due to their high conductivity and different electroactivity can be used as the main components in p−n organic-based heterojunctions.[19−22] However, one of the limitations of phthalocyanine-based devices is their low luminescence.[23] Co-depositing phthalocyanine with PTCD derivatives may enhance the Pc luminescence via energy transfer. It has been shown that energy transfer and luminescence depend on the molecular organization in the film.[24,25] Therefore, changes in film morphology,[26] induced through thermal annealing or vapor exposure,[27] may affect the emission characteristics of the films depending on the degree of mixing. We have previously reported that in mixed films of phthalocyanine−PTCD derivatives, a distribution of aggregates is obtained (detection of phase separation) as extracted from different spectroscopic and microscopic techniques.[28] In the present work, the absorption and emission properties of equimolar, 100-nm mass thicknesses, co-evaporated mixed films of TiOPc with BNPTCD and ClInPc with BNPTCD are reported for the first time. Also, BNPTCD (50 nm)/ClInPc (50 nm) and BNPTCD (50 nm)/TiOPc (50 nm) bilayers were fabricated as model systems with a well-defined interface. The molecular structures of the BNPTCD and phthalocyanines are given in Scheme 1.

The characteristic emission of a unique exciplex in the TiOPc−BNPTCD mixed film has been identified. The exciplex emission correlates with a high degree of mixing in the film. In contrast, but in agreement with previous findings for phthalocyanine−PTCD[29] mixtures, no exciplex emission was observed in the ClInPc−BNPTCD mixed film.[30]

**Scheme 1. Molecular Structure of TiOPc, ClInPc, and BNPTCD.**



## Experimental Section

The BNPTCD synthesis and characterization have been reported,[31] CA index name being 2,9-dineopentyl-anthra[2,1,9-def:6,5,10-d′e′f′] diisoquinoline-1,3,8,10(2H,9H)-tetrone. The materials were mixed in 1:1 and 2:1 (phthalocyanine:BNPTCD) molar ratio amounts and simultaneously deposited by co-evaporation from the same source onto silver mirrors (RAIRS), KBr plates (transmission IR), and Corning glass (UV and fluorescence measurements) with a deposition rate between 1 and 3 Å $s^{-1}$. The films were evaporated under a pressure of $10^{-6}$ Torr and the mass thickness (100 nm) was controlled by a quartz crystal balance. The same procedure was used in the fabrication of bilayer BNPTCD (50 nm)/phthalocyanines (50 nm) films. The UV−visible absorption spectra of the thin solid films were obtained on the Varian Cary 50 Scan UV−vis spectrometer. The micro-Raman and fluorescence spectra and global imaging were obtained with a Renishaw Research Raman Microscope System RM2000 equipped with a Leica microscope. The Raman and fluorescence spectra were recorded using the 514.5-nm argon ion laser line. The laser power at the samples was 57 $\mu$W. AFM measurements were carried out with a Topometrix TMX 2010 Discoverer instrument in contact mode. Transmission and RAIRS infrared spectra were recorded using a BOMEM DA3 FT-Infrared spectrometer with 1-$cm^{-1}$ resolution for the bulk (256 scans) and 4-$cm^{-1}$ resolution for the films (1000 scans). RAIRS measurements were recorded at an incident angle of 80°. Structural and morphological changes induced by thermal annealing in thin films of neat perylene tetracarboxylic diimide,[27,31] neat phthalocyanines,[32] and PTCD/phthalocyanine bilayer films[24] usually take place at temperatures over 120 °C. Therefore, to study the thermal effect on film structure, films were annealed at 150 °C under vacuum and at atmospheric pressure. The annealing time was 45 min.

## Results and Discussion

**A. Electronic Absorption Spectra**. The electronic absorption spectra of neat films of the materials, TiOPc, ClInPc, and BNPTCD, are shown in Figure 1. Electronic spectra recorded in the same spectral region as those of the neat film are shown in Figure 2a for TiOPc−BNPTCD mixed film recorded at room temperature and

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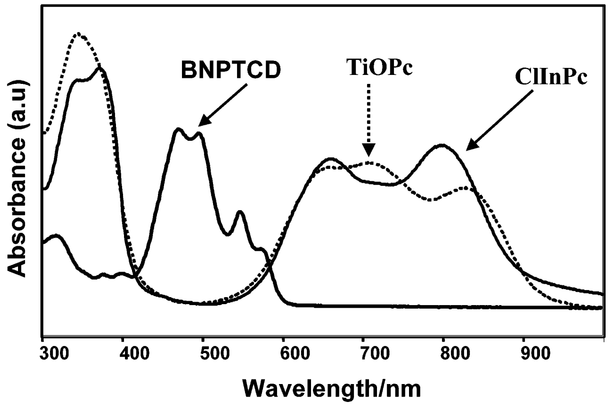

**Figure 1.** Electronic absorption spectra of the TiOPc, ClInPc, and BNPTCD materials.

after thermal annealing at 150 °C. The BNPTCD absorption bands maxima at 537 and 468 nm correspond to characteristic peaks of the $\pi-\pi^*$ transition in the PTCD moiety.[33] These bands are usually observed in amorphous PTCD films and disordered solids.[25,34] The absorption spectrum of TiOPc consists of a broad Soret band centered at 343 nm and a Q-band with maxima at 660 and 720 nm. This spectrum corresponds to that of amorphous TiOPc.[35] The electronic absorption spectrum shows no significant changes after thermal annealing.

The ClInPc−BNPTCD mixed film electronic absorption spectrum (Figure 2b) exhibits a similar profile to that of the TiOPc−BNPTCD at room temperature. However, thermal annealing of the ClInPc−BNPTCD mixed film shows the characteristic band splitting of well-ordered BNPTCD evaporated neat films, with peaks at 499, 466, 543, and 569 nm.[31] The ClInPc Soret band splits into two peaks at 340 and 380 nm, while the Q-band splits into two broad bands with maxima at 660 and 810 nm, in agreement with the spectrum of well-ordered evaporated ClInPc neat films.[36] Therefore, thermal annealing increases phase separation in the ClInPc−BNPTCD mixed film, and the molecules of each phase recover the molecular alignment found in their neat evaporated films. It is concluded that the TiOPc−BNPTCD shows a much greater degree of mixing than the ClInPc−BNPTCD and might be due to the stronger molecular interaction between species in the mixed film.

The absorption spectra of the BNPTCD/TiOPc and BNPTCD/ClInPc bilayer films shown in parts c and d, respectively, of Figure 2 are there to illustrate the behavior of “phase-separated” materials. Thermal annealing induces molecular realignment in the TiOPc and the ClInPc layers. The interaction at the interface in the BNPTCD/TiOPc bilayer is not comparable to that in the mixed film, which prevents phase separation and molecular realignment. Therefore, the TiOPc layer follows the behavior of neat evaporated films. The phase separation in ClInPc−BNPTCD mixed film is confirmed by comparison with the phase-separated bilayer absorption spectra. Similar effects may also be induced by solvent vapor annealing.[24,25]

**B. Emission Spectra**. The emission spectrum of the TiOPc−BNPTCD mixed film, excited with the 514.5-nm laser line, is illustrated in Figure 3a. The reference emission spectra of the TiOPc and BNPTCD neat films are also shown. The electronic emission spectrum of a thin neat film of TiOPc consists of a featureless band centered at 894 nm. The quantum efficiency of the phthalocyanine neat thin film’s emission is low compared to that of PTCDs. The BNPTCD film shows the characteristic strong fluorescence of PTCD derivatives,[37] a broad band (260-nm width) in the visible spectral region, with two maxima at 590 and 648 nm, assigned to the monomer and excimer emissions, respectively. In the emission spectrum of the TiOPc−BNPTCD mixed

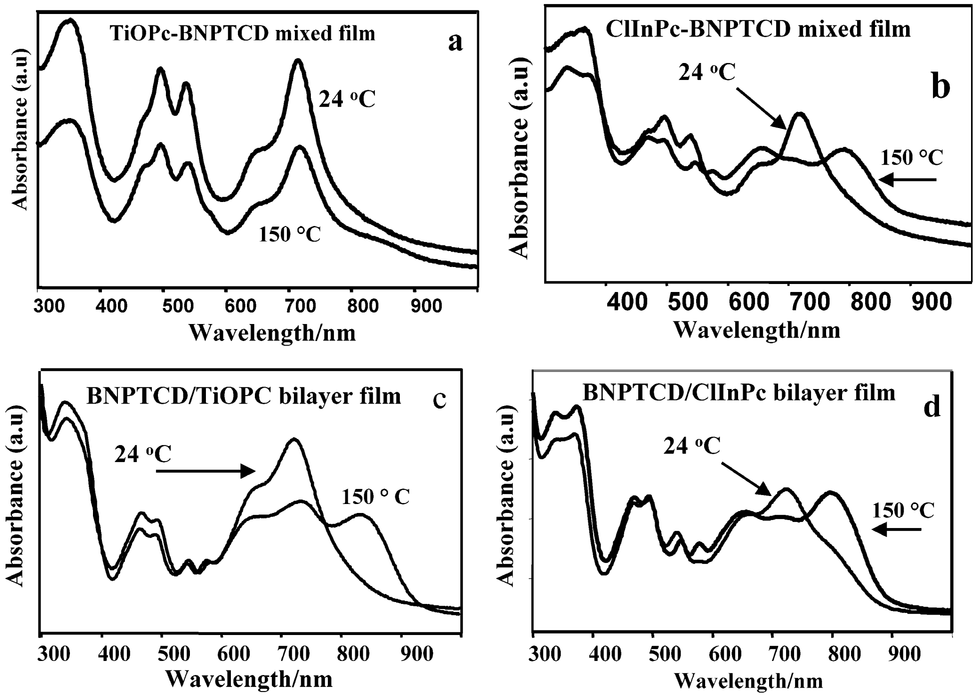

**Figure 2.** Electronic absorption spectra of the TiOPc−BNPTCD mixed film (a) and bilayer BNPTCD/TiOPc film (c) at room temperature and annealed at 150 °C. Electronic absorption spectra BNPTCD−ClInPc mixed film (b) and the bilayer film at room temperature and annealed at 150 °C (d).

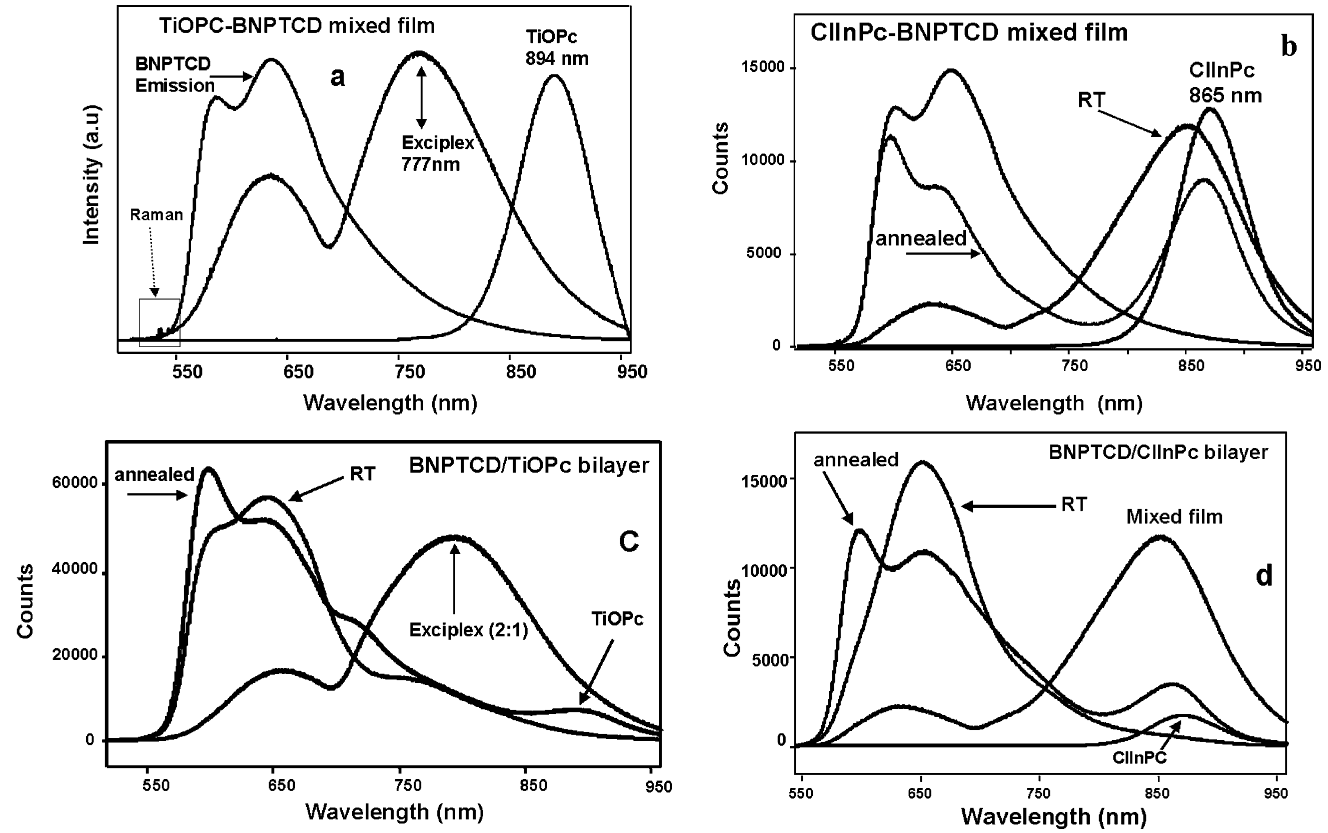

**Figure 3.** Emission spectra, excited with the 514.5-nm laser line, of the neat films and that of the TiOPc−BNPTCD mixed film showing the exciplex emission (a). Arbitrary units are used for the *y*-axis to show the weak emission from a neat TiOPc film. (c) Emission spectra of the BNPTCD/TiOPc bilayer film at room temperature and annealed at 150 °C, compared with the exciplex emission from a 2:1 molar ratio mixed film of TiOPc−BNPTCD. (b) Emission spectra of the ClInPc−BNPTCD mixed film illustrating the increase in the ClInPc emission due to the energy transfer process. The BNPTCD profile of the neat film has been divided by 5; the profile of the ClInPc neat film has been multiplied by 13. (d) Emission spectra of the BNPTCD/ClInPc bilayer film and that of the mixed film showing the effect of annealing on energy transfer. The weak emission spectrum of neat ClInPc film is also shown for comparison.

film (Figure 3a), two broad bands are clearly observed, with maxima at 645 and 777 nm. The 645-nm band corresponds to the BNPTCD excimer emission. However, the 777-nm band is new and does not correspond to the natural fluorescence of either of the two species. We have assigned this broad emission band to the exciplex emission. The lack of any band in the absorption spectrum of the mixed film that could be assigned to a complex formation between the molecules indicates that formation of the complex takes place only in the excited state and, therefore, it is not directly accessible from the ground state, consistent with the exciplex assignment.[12] The formation of these excited species must be the result of the significant spatial overlap between the molecular orbitals of the two species allowed by the high degree of mixing in the mixed film. The relative exciplex emission intensity is higher than that of the excimer band, which indicates that the exciplex formation is the main excitation deactivation path in the TiOPc−BNPTCD mixed film. The fact that the exciplex band is considerably blue-shifted (ca. 120 nm) with respect to the emission band of the TiOPc neat film indicates that the exciplex formation takes place at short distance and is induced by the strong interaction between components.[38] It was also found that the exciplex emission is observed after the mixed film had been thermally annealed. Changing the proportions in the mixture can control the exciplex formation. In a separate experiment a mixed film with a 2:1 (TiOPc−BNPTCD) molecular ratio was fabricated, which would increase the exciplex/excimer ratio. The observed emission for the latter film shows the corresponding decrease in the emission of the BNPTCD excimer band and an enhancement of the exciplex band intensity (as shown in Figure 3c).

The emission spectrum of the bilayer BNPTCD/TiOPc film is dominated by the intense broadband characteristic of the BNPTCD excimer fluorescence. However, a weak exciplex emission also appears as a broad shoulder at ca. 770 nm, which is due to exciplex formation at the bilayer interface (Figure 3c). Notably, the exciplex band, with the same relative intensity, is also observed after thermal annealing.

**ClInPc−BPTCD Emission.**The neat ClInPc thin film emission band is similar to that of TiOPc, but

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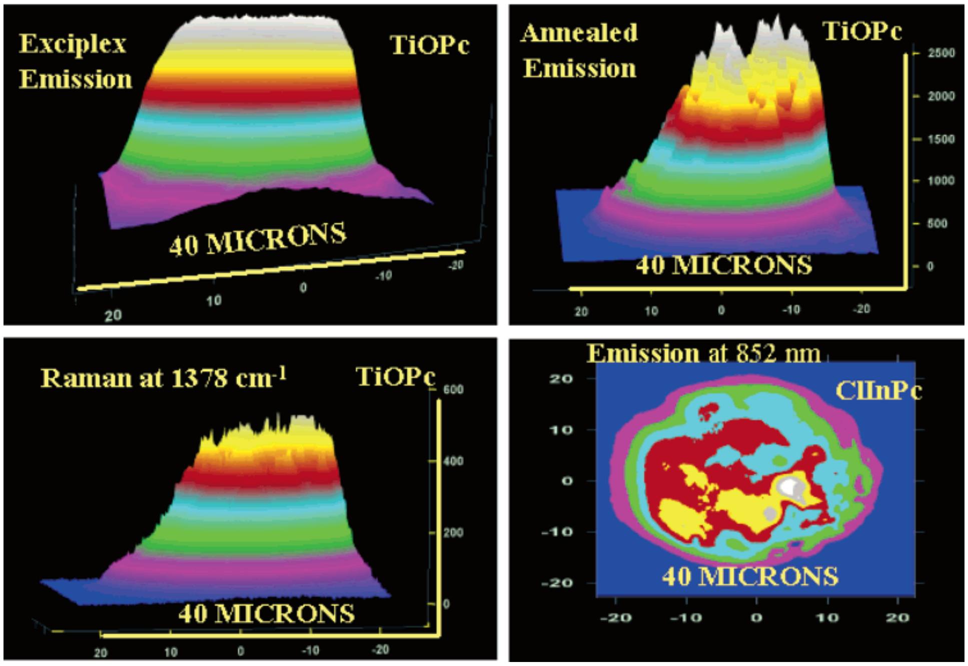

**Figure 4.** Three-dimensional image of the exciplex emission (at 780 nm) of TiOPc−BPTCD (top left) and Raman imaging (at 1378 cm$^{-1}$) (bottom left) of BNPTCD in the mixed film. Exciplex emission of the annealed TiOPc−BNPTCD mixed film at 150 °C (top right) and two-dimensional map of ClInPc emission in the annealed mixed film showing phase separation (bottom right).

centered at 865 nm. The ClInPc−BPTCD mixed film shows two emission bands centered at 852 and 631 nm (Figure 3b), which can be assigned to the ClInPc and BNPTCD emissions, respectively. There is no evidence of exciplex emission in these mixed films. However, the quenching of the BNPTCD fluorescence observed in these mixed films indicates an efficient energy transfer from BNPTCD to ClInPc as shown in Figure 2b. After thermal annealing the emission spectrum of the ClInPc−BNPTCD mixed thin film, also given in Figure 3b, showed a significant reduction of the energy transfer efficiency from the BNPTCD to ClInPc. The molecular realignment changes the film morphology, enhancing the natural deactivation pathways of the BNPTCD molecules and hindering the energy transfer.

The BNPTCD/ClInPc bilayer emission spectrum at room temperature (Figure 3d) is clearly dominated by the emission of the BNPTCD layer, and no significant energy transfer is observed. After thermal annealing, a modest increase in energy transfer is seen, and the intensity of the unshifted ClInPc emission is slightly amplified.

In conclusion, exciplex formation results from strong interaction between species and, thereby, requires a high degree of molecular mixing that allows for the proximity required for a $\pi-\pi$ molecular orbital interaction. In contrast, the energy transfer phenomenon can occur at larger distances and can be observed in phase-separated mixed films. The comparative analysis between the emission properties of mixed and bilayer films of TiOPc−BNPTCD and ClInPc−BNPTCD shows exciplex formation in the former and a dominant energy transfer process in the latter.

**C. Emission and Micro-Raman Global Imaging.** To illustrate the findings extracted from the electronic absorption and emission spectra, the global imaging technique (an option in our Micro-Raman system) is applied here to visualize the spatial distribution of exciplex formation and to provide a chemical image of the phase separation in mixed films. Global images were recorded using angled tuned dielectric filters at a given Raman wavenumber of the spectrum (1378 cm$^{-1}$) and at the center of the fluorescence band. The laser spot size is defocused and the scattered light from a large surface area is collected. A constant area of 40 $\mu$m$^2$ was used here to facilitate a visual comparison of results.

Global images from a 40-$\mu$m$^2$ surface area of the exciplex emission at 777 nm were recorded throughout the surface of the TiOPc−BNPTCD mixed film. A representative three-dimensional global image is shown in Figure 4 (top left). As can be seen, homogeneous distribution of the exciplex emission was observed in agreement with the nature of the mixed film. Exciplex emission is found throughout the film as a result of the strong molecular interaction between species conferred by the high degree of mixing.

Homogeneous mixing in the TiOPc−BNPTCD mixed film seen in the fluorescence imaging should also be seen in the Raman global images collected at a characteristic vibration wavenumber. The vibrational band in the BNPTCD Raman spectrum centered at 1378 cm$^{-1}$ was selected, and images were collected from 40-$\mu$m$^2$ surface areas. Again, a representative image was selected and is given in Figure 4 (bottom left), showing a homogeneous distribution of BNPTCD in the mixed film.

Global imaging can also be used to visualize the effect of thermal annealing on film properties. As can be seen in Figure 4 (top right), the effect of annealing on TiOPc−BNPTCD mixed film is noticeable in the global images and there is some degradation of the exciplex emission.

The effect of thermal annealing on ClInPc−BNPTCD mixed films is extensive phase separation, as can be seen in the two-dimensional cross-sectional map of the global image (Figure 4, bottom right) collected at the maximum of the ClInPc emission band. The inhomogeneity of the light distribution shows ClInPc domains

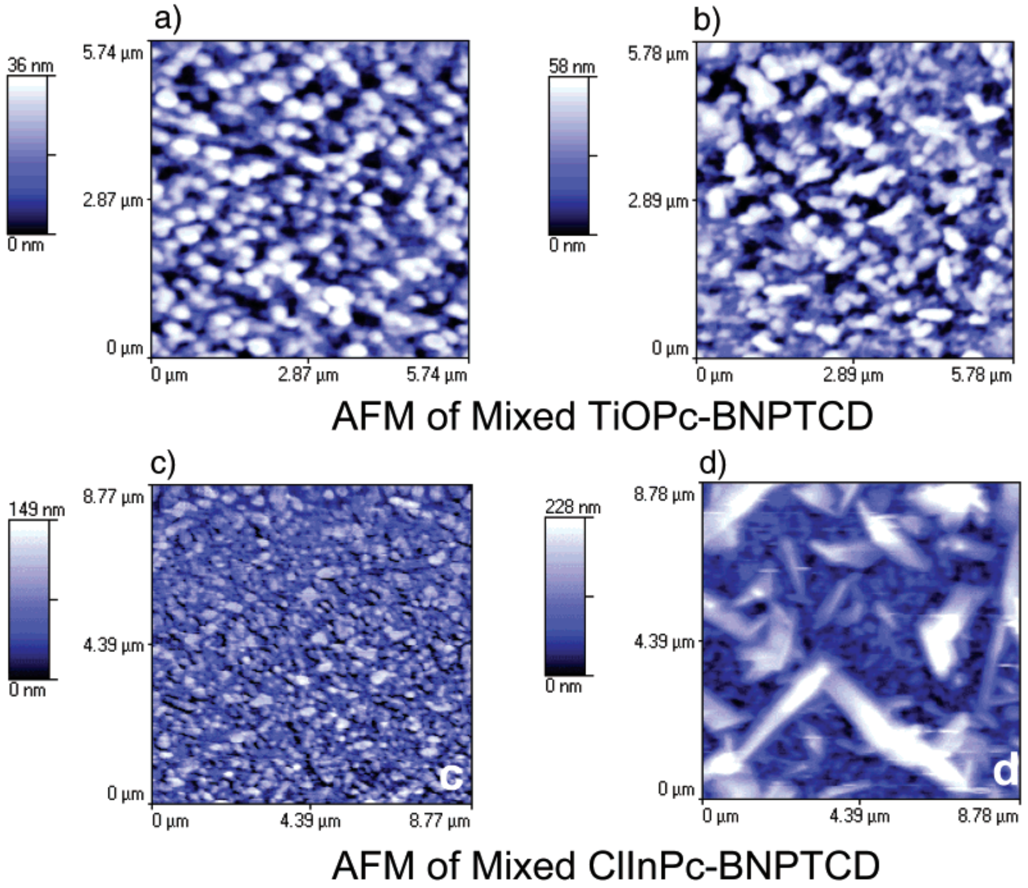

**Figure 5.** AFM topographical images of the TiOPc−BNPTCD mixed film (a) before and (b) after annealing. AFM topographical images of the ClInPc−BNPTCD (c) prior to annealing and (d) after annealing where the BNPTCD needle-shaped crystals are evident.

(light coloration) and dark sections of BNPTCD domains.

**D. AFM Measurements.** To complete the study of film morphology, several AFM images before and after thermal annealing of the TiOPc−BNPTCD mixed film were recorded. Thermal and solvent annealing of PTCD neat films lead to substantial change in film structure that are clearly observed and well-documented with topographical AFM images of such films.[27] During the annealing process, if the thermal energy added to the system overcomes the surface free energy, the molecules start a ripening process that leads to crystallization. This phenomenon has been observed in NSOM and AFM images of PTCD derivatives films. The film morphology changes from a small-sized lentil-like particle to the formation of isolated well-defined needle-shape crystals.[25,39] This evolution has also been seen in topographical images of TiOPc/perylenephenethyline.[24,25] However, the AFM images obtained from the TiOPc−BNPTCD mixed films (Figure 5) show that thermal annealing does not induce significant morphological changes and BNPTCD crystallization does not occur. The film before and after annealing presents a granular structure, and only slight increases of particle size (from 165 to 200 nm averages values), average surface roughness and annealing induces film porosity. Therefore, a high degree of mixing in TiOPc−BNPTCD mixed films is also supported by AFM measurements of thermal annealing.

In a parallel AFM analysis shown in parts c and d of Figure 5, the structure of the ClInPc−BNPTCD mixed film can be seen. The original ClInPc−BNPTCD mixed film that is shown in Figure 5c shows a granular morphology. However, thermal annealing induces drastic changes in film morphology, leading to the crystallization of BNPTCD, as can be clearly seen in Figure 5d. These changes in film morphology help support the conclusion of phase separation, leading to decreased energy transfer efficiency in annealed ClInPc−BNPTCD mixed films.

**E. Reflection−Absorption Infrared Analysis.** Infrared spectroscopy is a powerful tool for determining the molecular alignment in thin solid films.[40] Since the absorption of infrared radiation by a molecule is determined by the scalar product $E{\cdot}\mu$, where $E$ is the electric field of the electromagnetic radiation and $\mu$ the dynamic dipole moment, the observed intensities, for a thin solid film on metal surfaces, depend on the average molecular orientation and polarization properties of the light (direction of $E$) at the surface. The experimental observation of the "surface selection rules" for films on reflecting surfaces is accomplished using reflection−absorption infrared spectroscopy (RAIRS) and can be used to probe the average molecular orientation. The

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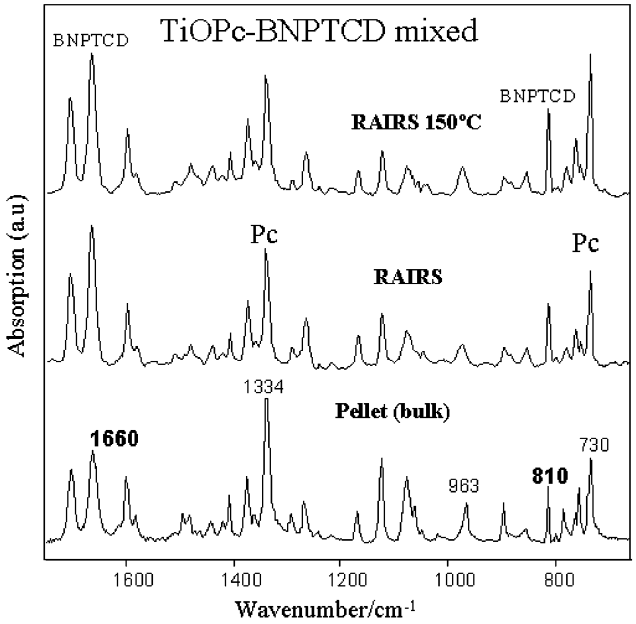

**Figure 6.** Reflection−absorption infrared spectra (RAIRS) of a TiOPc−BNPTCD mixed film before and after annealing. The transmission reference spectrum (pellet) of the mixture is at the bottom.

technique is, of course, valuable for extracting molecular orientation information of molecules adsorbed onto flat metal surfaces when the spectrum with a random distribution of molecules (pellet) is known and the vibrational fundamentals are well-assigned.

Thin solid films of TiOPc deposited at room temperature show packing with the Pc-macrocycle plane tilted with respect to the substrate, changing to a preferential face-on molecular alignment after thermal annealing.[41] In the ClInPc neat evaporated films an unmistakable face-on Pc-macrocycle orientation is observed.[41] Transmission FT-IR of randomly dispersed Pc in a KBr pellet (reference spectrum), and RAIRS of the mixed films deposited onto silver mirrors, was recorded to correlate changes in molecular organization (due to thermal annealing) with changes in the emission spectra. The vibrational work focused on the change of the relative intensity ratio observed for the 1334 cm$^{-1}$ C−N in-plane stretching (or the 1120 cm$^{-1}$ C−H in-plane bending) and the 730 cm$^{-1}$ out-of-plane vibrational modes of the TiOPc shown in Figure 6. In the case of the TiOPc, the Ti═O stretching mode at 963 cm$^{-1}$ could also be used. For BNPTCD, the relative intensity of the fundamental vibrations at 810 cm$^{-1}$, C−H wagging out of the PTCD plane, and the symmetric and antisymmetric C═O stretching modes (in the PTCD plane) at 1660 and 1698 cm$^{-1}$, were used. For instance, the ratio of relative intensities of characteristic out-of-plane/in-plane ($I_{732}$/$I_{1330}$) vibrational modes observed for ClInPc is 0.9 in the KBr pellet spectrum (random orientation), but it is 4.2 in the RAIRS spectrum, indicating a face-on ClInPc organization in the film. The latter can also be seen in mixed films as shown in Figure 6.

The reference KBr pellet spectrum, RAIRS at room temperature, and RAIRS of the annealed TiOPc-BNPTCD mixed film are shown in Figure 6. The reference and the RAIRS spectra at room temperature present a similar pattern of relative intensities, indicating that neither of the components shows a preferential molecular orientation in the mixed film. This high degree of disorder of the mixed evaporated film (or lack of large aggregates with preferential molecular stacking) is in good agreement with the unique molecular mixing of this film. Thermal annealing provokes slight changes in the film molecular arrangement, as can be seen in the RAIRS spectrum after annealing at 150 °C in Figure 6, in total agreement with the results from global imaging of mixed films. The relative increase in intensity of the 730-cm$^{-1}$ out-of-plane bending peak of TiOPc with respect to the 1334-cm$^{-1}$ C−N in-plane mode indicates some reorientation of the TiOPc molecules to edge-on alignment. Correspondingly, the relative intensities of the BNPTCD modes remain unchanged. From the infrared spectral data, it can be extracted that the thermal annealing does not induce significant molecular reorientation that could lead to characteristic alignment seen in neat films. Therefore, infrared spectroscopy provides information about the film structure that support and explain the findings extracted from the UV−vis absorption, emission spectra, and global imaging.

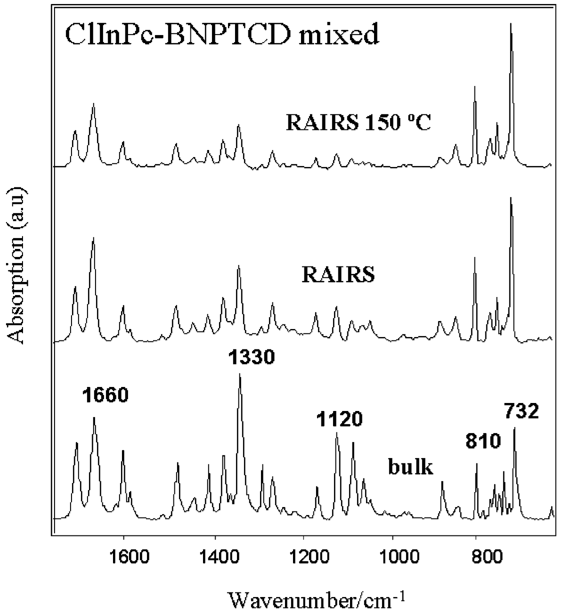

**Figure 7.** Reflection−absorption infrared spectra (RAIRS) of a ClInPc−BNPTCD mixed film. The transmission reference spectrum (pellet) of the mixture is at the bottom.

A very different conclusion can be extracted from the analysis of the transmission and RAIRS spectra of the ClInPc−BNPTCD mixed films shown in Figure 7. The high relative intensity of the 732-cm$^{-1}$ C−H out-of-plane wagging mode in RAIRS shows that the ClInPc molecules have a preferential face-on Pc orientation, as is found in their evaporated neat films. Thermal annealing further increases the intensity difference between the 732-cm$^{-1}$ C−H out-of-plane wagging and the 1330-cm$^{-1}$ C−N in-plane mode in favor of the C−H out-of-plane wagging, indicating that ClInPc molecules have a predominant face-on orientation. The molecular alignment is correlated with a lower degree of mixing in the mixed film, formation of large aggregates, with increasing phase separation between components. In addition,

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[41] Aroca, R.; Thedchanamoorty, A. *Chem. Mater.* **1995**, *7*, 69−74.

there is a large increase in the intensity of the 810-cm$^{-1}$ out-of-plane bending mode of the BNPTCD molecules in comparison to the 1660-cm$^{-1}$ C═O stretching in-plane mode, similar to the increase observed in annealed neat BNPTCD films. In summary, the infrared analysis provides information about the film structure that explains phase separation in the mixed ClInPc–BNPTCD films produced by thermal annealing. The separated phases in the mixed film adopt a molecular organization that agrees with the alignment found in the corresponding neat films.

## Conclusions

The first example of phthalocyanine–perylene derivative exciplex formation is reported. TiOPc–BNPTCD co-evaporated films allow exciplex emission to be observed due to a high degree of molecular mixing. Thermal annealing has a minor effect on the TiOPc–BNPTCD film structure and on excimer emission, in correspondence with the conservation of the degree of mixing in the film. A visualization of the emission properties of the mixed films is provided using global imaging techniques complemented with Raman imaging. The infrared reflection–absorption data provide information about the film structure and molecular organization that correlates with the properties of the exciplex emission. In a parallel investigation in which ClInPc substitutes the TiOPc, there was no evidence of exciplex formation for co-evaporated ClInPc–BNPTCD mixed films. Emission data obtained for ClInPc–BNPTCD mixed films revealed high energy transfer efficiency from the absorber BNPTCD to the emitter ClInPc. The infrared data showed that there is a low degree of mixing in ClInPc–BNPTCD films and that thermal annealing increases phase separation. The results of this work can contribute to the discussion of exciplex formation in small-molecular-weight thin films and the information gained may be practical to thin film device applications.

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