

Perylene Tetracarboxylic–Phthalocyanine Mixed Thin Solid Films. Surface-Enhanced Resonance Raman Scattering Imaging Studies

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The analytical application of surface-enhanced Raman scattering and surface-enhanced resonance Raman scattering (SERRS) in micro-Raman global imaging of mixed films is demonstrated by the use of laser powers below 1 mW and time acquisitions of a few seconds. SERRS eliminates the need for high-power lasers to record global images. Thin solid mixed films of phthalocyanine (chloroindium, chlorogallium, copper, cobalt, zinc, and metal-free phthalocyanine), bis(*n*-propylimido)perylene, and thio-bis(*n*-propylimido)perylene derivatives were fabricated by vacuum co-evaporation onto glass and silver island films. The spatial distribution or degree of mixing in the co-evaporated films on silver was probed by using SERRS. The micro-Raman spectra and images were recorded by using laser lines at 514.5, 633, and 780 nm. The monochromatic light, with frequency in and out of resonance with the dye's electronic absorption, allows selective observation of the corresponding material in the mixed film.

Introduction

Mixed films of phthalocyanine and perylene derivatives have promising applications in heterojunctions for semiconductors and photovoltaic cells. Tang was the first to report on a two-layer organic photovoltaic cell consisting of copper phthalocyanine and a perylene derivative.¹ A detailed investigative study into the optical and electrical properties of heterojunctions of similar mixtures soon followed.^{2,3} The implications of doping on the physical and chemical properties of mixed films have been realized. Rudiono et al. have reported on the effect of perylene doping of copper phthalocyanine on morphology and photovoltaic performance. It was found that perylene doping improved the photovoltaic performance of CuPc due to the expansion of its light absorption spectrum, though heavy doping deteriorated the photovoltaic characteristics of the cell.⁴ Similarly, fullerene doping of titanil phthalocyanine and a perylene pigment heterojunction has been reported to exhibit a higher quantum yield for charge carrier photogeneration than an undoped TiOPc layer.⁵ Electroabsorption studies of the electric fields in bilayer molecular organic cells

made from zinc phthalocyanine and a methyl-substituted perylene pigment have also been performed.⁶ In this investigation, it was concluded that the electroabsorption spectrum of the heterojunction is different from that of the bulk of the two layers, due to a strong electric field at the interface. Another differentiating characteristic of bulk and thin films of phthalocyanine and perylene was found by the investigation of the phases of vanadyl phthalocyanine obtained through a sequence of depositions.⁷

There are numerous combinations of perylene and phthalocyanine derivatives that may be formed into heterojunctions. The study of photoelectrical conversion using these materials has been an active area of research in organic devices.^{8–15} Recently, even the absorption of visible light by submicrometer (up to 50 nm

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effective thickness) neat films of Pc and PTCd materials has been revisited.¹⁶ In some recent work, we have presented the results of micro-Raman studies of mixed films of CuPc and CoPc with bis(*n*-propylimido)perylene (bisPTCD).¹⁷ Molecular mixing of these dyes could be possible because the two chromophores, Pc and PTCd, have very similar molecular dimensions. The long molecular axis of PTCd has almost the same length (ca. 12 nm) as the side of the Pc square (ca. 13 nm). Here, we report the micro-Raman imaging studies of co-evaporated mixed films of phthalocyanine and perylene derivatives as determined by using surface-enhanced resonance Raman scattering (SERRS) and micro-Raman imaging.

Experimental Section

Materials. The spectra and syntheses of bis(*n*-propylimido)perylene (denoted as bisPTCD, $M_w = 474.516 \text{ g mol}^{-1}$) and thio-bis(*n*-propylimido)perylene (denoted as thioPTCD, $M_w = 504.564 \text{ g mol}^{-1}$) have been previously reported.^{18,19} Cobalt phthalocyanine (CoPc, $M_w = 571.47 \text{ g mol}^{-1}$), copper phthalocyanine (CuPc, $M_w = 576.083 \text{ g mol}^{-1}$), zinc phthalocyanine (ZnPc, $M_w = 577.917 \text{ g mol}^{-1}$), and metal free phthalocyanine (H_2Pc , $M_w = 514.55 \text{ g mol}^{-1}$) were purchased from Kodak. Chlorogallium phthalocyanine (ClGaPc, $M_w = 617.71 \text{ g mol}^{-1}$) and chloroindium phthalocyanine (ClInPc, $M_w = 662.81 \text{ g mol}^{-1}$) were synthesized at the Xerox Research Centre of Canada. The molecular structures are shown in Figure 1. Mixed films were fabricated by mixing equimolar amounts of the following perylene and phthalocyanine pigments: bisPTCD with ClGaPc, ClInPc, CoPc, CuPc, H_2Pc , and ZnPc and thioPTCD with ClGaPc, ClInPc, CoPc, CuPc, H_2Pc , and ClInPc.

Thin Film Preparation. The substrates used for thin film preparation were transparent and pre-cleaned Borosilicate slides (Baxter Cat. M6145). They were cleaned by rubbing with ethanol and subsequent drying under a continuous flow of dry nitrogen gas. Metal deposition was performed in a Balzers vacuum system evaporator. Silver shots (Aldrich 20, 436-6) were thermally evaporated from a cupped tungsten boat by using a Balzers BSV 080 glow discharge/evaporation unit. The background pressure was nominally 10^{-6} Torr. On a substrate, preheated to $200 \text{ }^\circ\text{C}$, silver was deposited at a rate of 0.2 nm s^{-1} to a total mass thickness of 6 nm. This deposition rate was allowed to stabilize before the shutter was opened. Film thickness and deposition rate were monitored by using a quartz crystal oscillator. The bisPTCD and various phthalocyanine derivatives were mixed in equimolar amounts, and the mixture was co-evaporated onto silver island films (mass thickness of 6 nm). The evaporation system used was of the same setup aforementioned, with the exception that the substrate was not heated. The mixture was evaporated from tantalum boats at room temperature, with a deposition rate of 0.2 nm s^{-1} . The bulk density employed for the bisPTCD/Pc-derivative mixture was 1 g cm^{-3} . The same procedure was applied to the thioPTCD/Pc-derivative mixture.

Film Characterization. The UV-visible (UV-vis) spectra of thin solid films and solutions were obtained on the Varian Cary 50 Scan UV-vis spectrometer. The SERRS, mapping, and global imaging were obtained with a Renishaw Research Raman microscope system RM2000 equipped with a computer-controlled three-axis encoded (*XYZ*) motorized stage with a minimum step of $0.1 \text{ } \mu\text{m}$. The RM2000 uses a Leica microscope (DMLM series). The spectrum was measured by using a Peltier

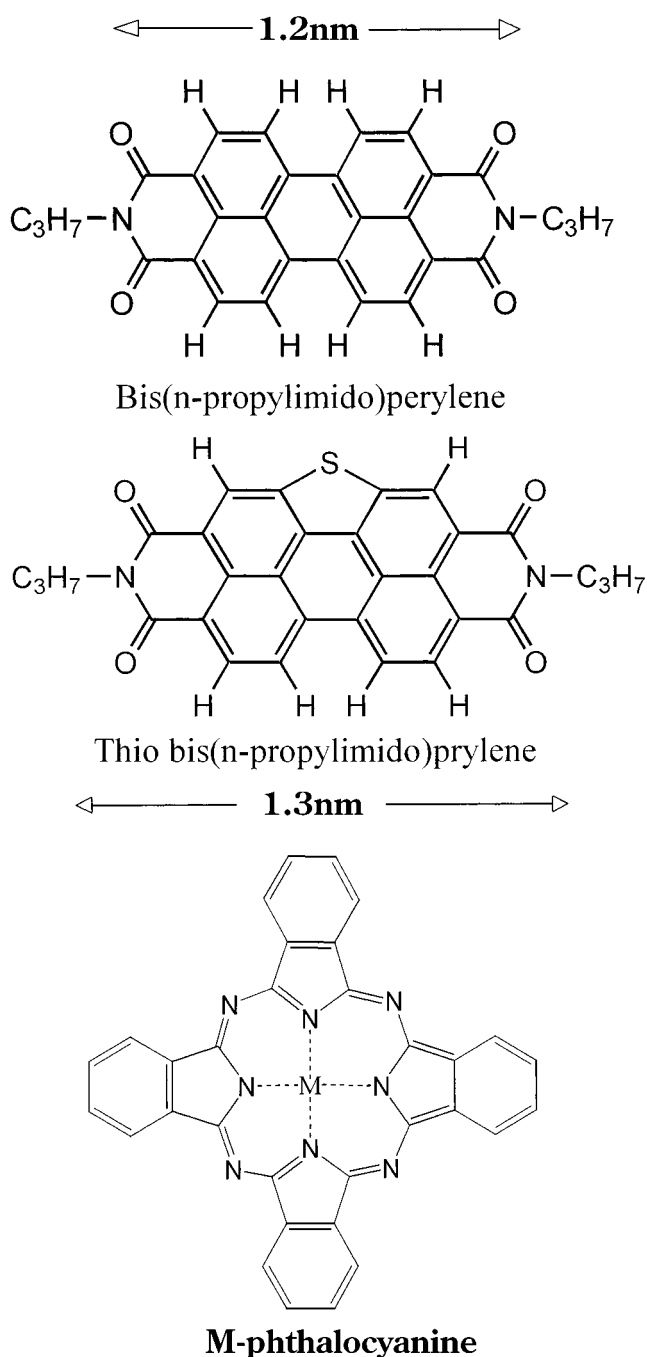


Figure 1. Molecular structure of MPC and PTCd molecules used in this work.

cooled ($-70 \text{ }^\circ\text{C}$) CCD array. Three laser lines were used for the excitation of the inelastic light scattering: 514.5, 633, and 780 nm. The laser power at the sample was varied between $20 \text{ } \mu\text{W}$ and 1 mW. Raman imaging was obtained by point-to-point sampling, where the laser spot size or the collection optics define the spatial resolution of the image. As the image consists of a sequence of single-point Raman spectrum acquisitions, the collection time is usually on the order of a few minutes to a few hours depending on the sampling area. Global imaging based on the light distribution in a wide field is achieved by collecting the scattering for a selected vibrational band over the entire illuminated area. The result is a sample image based on spectroscopic information from which the spatial distribution of a particular component may be extracted. Unlike point-to-point sampling, the acquisition of a two-dimensional image at one Raman shift is rapid (seconds) as a large number of samples spots are observed simultaneously. Furthermore, since global imaging uses a weakly

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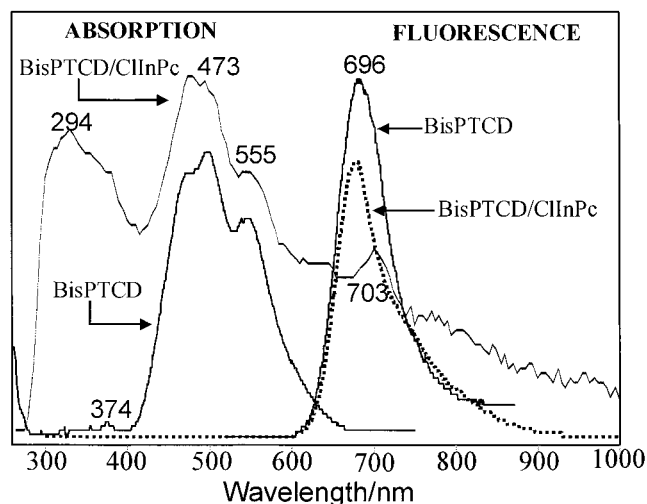


Figure 2. Electronic absorption and emission spectra of thin films of bisPTCD and mixed bisPTCD/ClInPc.

defocused laser beam, the power density is much lower than that in a single-point acquisition and reduces the risk of sample damage. Global images of the SERRS signal from mixed films of bisPTCD or thioPTCD and various phthalocyanine derivatives on silver island films were obtained by using the 633 nm laser line and the filtered Raman scattered light from the fundamental vibrational wavenumber center at ca. 1300 cm^{-1} for bisPTCD, 1380 cm^{-1} for thioPTCD, and ca. 680 cm^{-1} for phthalocyanines.

Results and Discussion

Absorption and Fluorescence. The absorption spectrum of a thin solid film of bisPTCD evaporated onto KBr substrate shows strong absorption signals at 374, 468, 501, and 547 nm as previously reported and shown in Figure 2.¹⁸ Similarly, the absorption spectrum of a thin solid film of thioPTCD contains maxima at 449, 480, and 519 nm (not shown).¹⁹

Since the electronic absorption spectra are sensitive to the molecular environment and even film thickness, a comparison of the spectra of neat bisPTCD and Pc with the mixed bisPTCD/Pc films spectra may show the effect of mixing in the electronic spectra of both PTCD and Pc components. The Soret band of the phthalocyanine moiety, appearing in the 320–340 nm regions in the mixed films, overshadows the secondary electronic absorption observed at 374 nm for bisPTCD films. The 0, 0 electronic transition observed in the bisPTCD films at 547 nm appeared red-shifted in the absorption spectra of all mixed films. The characteristic phthalocyanine Q-band was observed within the 610–620 nm spectral²⁰ region of absorption spectra of the mixed films that were investigated, one exception being the bisPTCD/ClInPc mixed film in which it was observed at 703 nm. The emission spectra of thin solid films of bisPTCD and thioPTCD have been previously reported.^{18,19} The broad structureless emission spectra, with Stokes-shifted maxima relative to the absorption origin, are characteristics for excimer-forming crystalline thin films of PTCDs.^{21,22} This characteristic broad excimer emission

is observed at 696 nm for a thin solid film of bisPTCD. In comparison, the excimer emission observed in all bisPTCD/Pc mixed films spectra showed a blue-shifted emission maximum, with the exception of bisPTCD/ZnPc in which the maximum is red-shifted to 715 nm. In general, changes in the absorption and emission spectra indicate that bisPTCD aggregation does not follow the same pattern present in the neat evaporated films. However, the observed spectra allow one to conclude that the bisPTCD aggregates are present in the mixed films, and thereby there is no spectral evidence for molecular mixing.

The absorption spectra of the thioPTCD/Pc mixed films, similar to those obtained for bisPTCD/Pc mixed films, contain characteristic absorption bands of both the perylene and phthalocyanine species. The phthalocyanine Soret band was observed in the 300–390 nm spectral region for all thioPTCD/Pc mixed films. The 0–0 thioPTCD electronic transition band was observed to be red-shifted in all thioPTCD/Pc mixed films with the exception of thioPTCD/ClInPc and thioPTCD/ZnPc mixed films where the absorption band was blue-shifted.

The fluorescence spectrum of thin solid films of thioPTCD reveals a broad emission band centered at 641 nm. The emission spectra of all thioPTCD/Pc mixed films that were investigated had maxima that were red-shifted to that observed for thioPTCD. The opposite was observed for the majority of the bisPTCD/Pc films. In conclusion, there is strong evidence of aggregation of thioPTCD in mixed films supporting the idea of mixed films formed by aggregates of both components with minimal molecular mixing.

Raman and Surface-Enhanced Raman Spectra. The vibrational spectra of metal phthalocyanines and metal-free phthalocyanine have been assigned.^{23–26} Similarly, the vibrational analyses of bisPTCD and thioPTCD have been reported.^{18,19} With the use of local symmetry arguments, the discussion of the vibrational assignments of bisPTCD and thioPTCD can be restricted to that of the parent PTCD chromophore that can be found in parent molecules such as PTCDI.²⁷ Since PTCD is a large planar moiety, it is reasonable to assume that changes in the polarizability ellipsoid due to the out-of-plane vibrational modes are relatively small and that in-plane stretching and deformation ring modes represent the most intense Raman bands in the Raman spectra. The observed fundamentals for both PTCD molecules in mixed films are listed in Table 1. The observed spectra of the mixed films containing ClInPc have been chosen to illustrate the results.

The resonant Raman scattering (RRS) and SERRS spectra of the mixed film bisPTCD/ClInPc obtained with the 514.5 nm laser line and the baseline corrected spectra are presented in Figure 3. The fundamental mode observed at 542 cm^{-1} is due to the perylene ring deformation. The C–H bend is observed at 1084 cm^{-1} , while perylene ring stretches appear at $1291(\text{sh})$, 1302 ,

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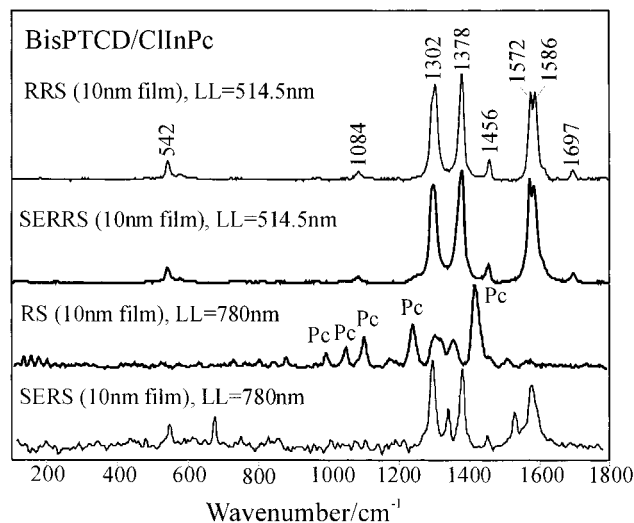


Figure 3. RRS, SERRS, RS, and SERS spectra of mixed thin solid films of bisPTCD/ClInPc.

Table 1. Assignments of Characteristic PTCDFrequencies Observed with the 514.5 nm Laser Line in Mixed Films of BisPTCD/ClInPc and ThioPTCD/ClInPc, Respectively

characteristic frequencies (cm^{-1})		
bisPTCD	thioPTCD	assignment
542	520	ring def
1084	1076	C-H bending
1291	1245	ring str
1302	1313	ring str
1378	1393	ring str
1456	1536	ring str
1572	1577	C=C str
1586	1620	C=C str
1697		C=O str

Table 2. Assignments of Characteristic Pc Frequencies Observed with the 780 nm Laser Line in Mixed Pc/PTCD Films

characteristic frequencies (cm^{-1})							
ClInPc	ClGaPc	CoPc	CuPc	ZnPc	H ₂ Pc	assignment	
	1608	1607			1606	benzene stretch	
1594	1592	1595	1591	1588	1594	benzene stretch	
1530	1529	1534	1529			isoindole stretch	
1453	1453	1452	1451	1454	1452	isoindole stretch	
1439	1430	1431	1430		1430	isoindole stretch	
1341	1341	1336	1335		1339	pyrrole stretch	
1141	1142	1137	1141		1140	pyrrole breathing	
1007	1006	1008	1007	1009	1004	C-H bend	
829	830	832		823	835	macro stretch	
677	677	682	679	677	677	macro breathing	
578	592	590	590	607	596	benzene def	

1378, and 1456 cm^{-1} . The ring C=C stretches are observed at 1572 and 1586 cm^{-1} , and the symmetric C=O stretch is at 1697 cm^{-1} . The SERRS spectrum obtained for this mixed film is clearly the enhanced version of the RRS spectrum and occurs when the PTCDF moiety is physisorbed onto the silver island substrate. To be physically adsorbed is taken to mean that there is no strong interaction (bonding) of the organic with the metal surface. In summary, at 514.5 nm excitation the RRS effect determines that the RRS and SERRS spectra of mixed films are completely dominated by the PTCDF moiety.

The Raman scattering (RS) of the mixed film of bisPTCD/ClInPc taken with the 780 nm laser line is also

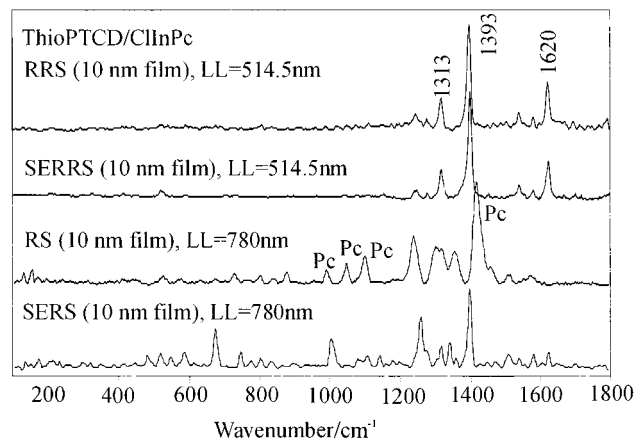


Figure 4. RRS, SERRS, RS, and SERS spectra of mixed thin solid films of thioPTCD/ClInPc.

presented in Figure 3. It becomes apparent on comparing the Raman spectra of this mixed film that the spectrum at 780 nm (RS) contains characteristic bands of both ClInPc and bisPTCD. In the RS spectrum, the most intense characteristic vibration observed at 1453 cm^{-1} belongs to the ClInPc moiety. The observed fundamentals for all Pc molecules in the mixed films are listed in Table 2. The surface-enhanced Raman scattering (SERS) spectrum of the mixed film, obtained with the 780 nm line, also shown in Figure 3, consists of a combination of ClInPc and perylene chromophore vibrations. However, the intensity of the bisPTCD SERS is again higher than that of the Pc molecule. Therefore, characteristic vibrations of the perylene moiety are used to discuss the SERS (780 nm) spectrum in an attempt to extract the effect of intermolecular interactions from the mixed film spectra. The predominant perylene bands in the SERS (780 nm) spectrum are observed at 1689, 1594, 1577, 1439, 1379, 1295, and 531 cm^{-1} . Taking the 531 cm^{-1} band as a reference, a comparison of the SERS (780 nm) to the RS spectra of bisPTCD/ClInPc mixed films indicates an increase in the relative intensities of four in-plane ring-stretching vibrations, in particular in that of the 1577 cm^{-1} vibration. Furthermore, in the SERS (780 nm) spectrum, the full width at half-maximum (fwhm) remained constant for all vibrational bands with the exception of 1379 and 1439 cm^{-1} . In the RS spectrum, the bandwidth doubles for the 1379 and 1439 cm^{-1} bands. This indicates the presence of doublets, not resolved in the spectrum due to band overlap. When the vibrational band at 542 cm^{-1} is used to normalize the spectra obtained with the 514.5 nm laser line, the relative intensities of the C-H bend and C=C stretching vibrational bands, at 1084 and 1586 cm^{-1} , respectively, decreased in the SERRS spectrum with respect to the RRS spectrum. A comparative analysis of the fwhm bandwidths shows that the bandwidth of the 1295 cm^{-1} vibrational band in the SERS (780 nm) spectra is double relative to that in the RRS spectrum.

Relative intensities of the characteristic perylene vibrational bands, normalized to the perylene ring deformation band at 542 cm^{-1} , were used to follow the trend in the observed Raman spectra. The relative intensities of perylene vibrational bands at 1084, 1302, 1378, and 1456 cm^{-1} are greater in the RS spectrum than that in the RRS spectrum for all mixed films,

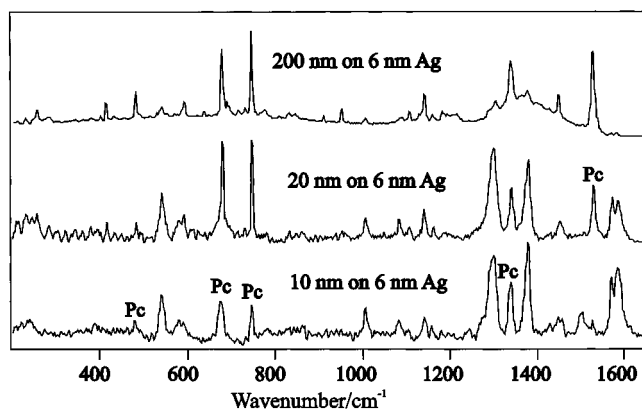


Figure 5. Thickness dependence of the SERS spectra of mixed solid films of bisPTCD/CuPc evaporated onto 6 nm Ag, recorded with the 780 nm excitation laser line.

bisPTCD/ZnPc having the greatest difference in relative intensities. For the ring-stretching vibrations at 1572 and 1586 cm^{-1} , the RRS spectrum has greater relative intensity than the RS spectrum for bisPTCD/Pc mixed films containing ClInPc, ClGaPc, CoPc, and CuPc. The exceptions being H_2Pc and ZnPc where the relative intensity of the 1572 cm^{-1} band in the RS spectrum is more intense than that in the RRS spectrum. Finally,

the C=O stretching vibration at 1702 cm^{-1} was observed only for mixed systems containing ClInPc, ClGaPc, CoPc, and H_2Pc . Of these systems the relative intensity for this band was more intense in the RS spectrum than in the RRS spectrum for mixed films of ClInPc, CoPc, and H_2Pc .

The spectra of the mixed film thioPTCD/ClInPc obtained with the 514.5 nm laser line are presented in Figure 4. The most intense bands observed are attributed to the perylene moiety at 1313, 1393, and 1620 cm^{-1} respectively. The RS spectrum of the mixed film of thioPTCD/ClInPc taken with the 780 nm laser line is also presented in Figure 4. The RS spectrum of the mixed films contains characteristic frequencies of both thioPTCD and ClInPc.

The SERS spectrum of the mixed film, obtained with the 780 nm line, is also shown in Figure 4. The SERS (780 nm) spectrum is similar to the RS spectrum, and the perylene bands are observed at 1699, 1620, 1577, 1397, and 1313 cm^{-1} . In the SERS (780 nm) spectrum, the fwhm remained constant for all perylene vibrational bands with the exception of the 1577 cm^{-1} band.

A similar approach in analysis was utilized for the other thioPTCD/MPc mixed films that were studied. The most noteworthy system is that of the thioPTCD/CoPc mixed films, in which there are relative intensity

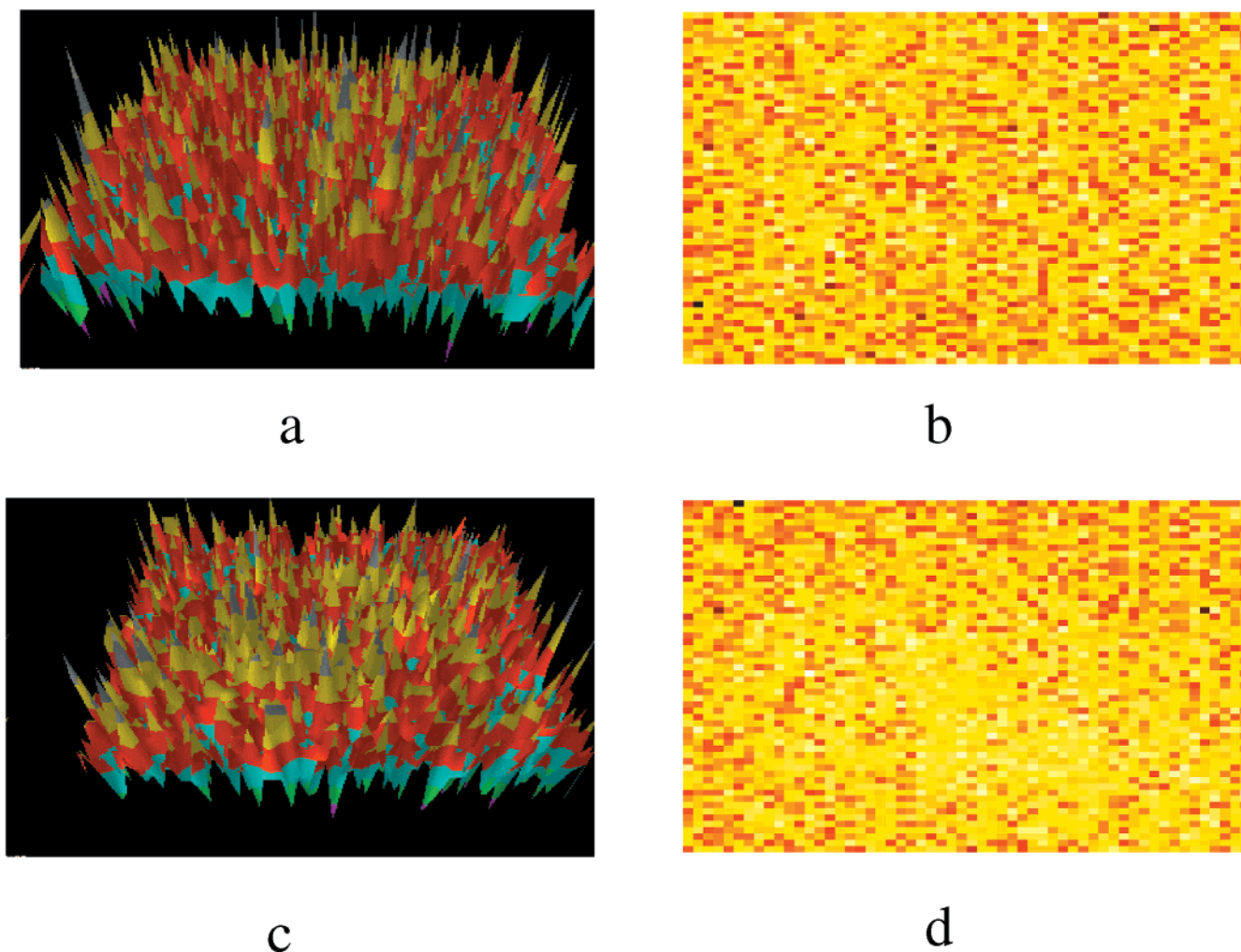


Figure 6. Global field images (6a and 6c) and point-to-point bit map images (6b and 6d) of mixed films of bisPTCD/ClInPc and thioPTCD/ClInPc, respectively.

deviations when comparisons are made between the RRS and the SERRS spectra and the RS and the RRS spectra of this mixture. Surprisingly, a comparison of the RS to RRS spectra of thioPTCD/CoPc mixed films reveals no change in fwhm bandwidths.

The extent of the spectral changes on the perylene moiety upon mixing with phthalocyanine was deduced by comparing relative intensities and fwhm bandwidths for Raman spectra of neat films of bisPTCD and thioPTCD. Such an analysis reveals similar deviations (for RS, SERS, RRS, and SERRS) in both relative intensities and bandwidths that are observed for the characteristic vibrational bands of the perylene chromophore in the neat films. Therefore, the perylene moiety in mixed films appears to retain the same molecular organization as in the neat film. This provides conclusive evidence for a lack of molecular mixing between phthalocyanine and perylene in these co-evaporated mixed films.

Optimum Film Thickness for SERRS. It is well-known that the first monolayer on a silver roughened surface dominates the SERS spectrum. The SERS spectra of mixed films of CuPc and bisPTCD with varying thickness, taken with the 780 nm excitation laser line, are shown in Figure 5. The 10 nm mixed film is considered to be an ultrathin film, while the 200 nm mixed film is regarded as a thick film. The SERS spectrum of the 10 nm CuPc/bisPTCD co-evaporated mixed film contains characteristic vibrational bands of both the perylene and phthalocyanine chromophores. Thus, the SERS effect enhances the scattering from both phthalocyanine and perylene molecules to an equal extent. However, as the thickness of the mixed films increases, the characteristic phthalocyanine vibrational bands become dominant. This is due to the fact that the contribution of the RRS effect of the phthalocyanine chromophore to the SERS spectra is more significant than that of the SERS effect. It can therefore be concluded that ultrathin mixed films (ca. 10 nm mass thickness) are appropriate for SERS and SERS imaging studies. The spectra of thicker films do not correspond to surface-enhanced spectra and become dominated by the signal of the bulk material.

SERRS Imaging of PTCD/Pc Mixed Films. Global images of the SERRS signal from mixed films of bisPTCD and various phthalocyanine derivatives as well as thioPTCD/Pc on silver island films were obtained using the 633 nm laser line. The global images from the mixed film samples were captured using the filtered Raman scattered light of the fundamental vibrational wavenumber at 1300 cm^{-1} for bisPTCD, at 1380 cm^{-1} for thioPTCD perylene, and at 680 cm^{-1} for phthalocyanine. The SERRS spectrum is seen on the background of a weak fluorescence. Consequently, for the

point-to-point mapping shown in parts b and d of Figure 6, we selected a baseline corrected intensity to avoid the fluorescence background.

The global field images shown in parts a and c of Figure 6 were taken from a $20\text{ }\mu\text{m}^2$ area. After the filtered spectrum in the selected region (ca. 1300 cm^{-1}) is recorded, the global images are collected with an acquisition time of seconds. A large number of these images are recorded by scanning large sections of the film. Representative images were selected (parts a and c of Figure 6) to illustrate the three-dimensional distribution of the bisPTCD SERRS signal from the mixed film on silver islands. The bisPTCD/ClInPc film presents a homogeneous distribution of aggregates of bisPTCD (and ClInPc) in the film as shown in the three-dimensional image (Figure 6a), where the bright coloration corresponds to the higher relative intensity of the SERRS signal from the bisPTCD center at 1300 cm^{-1} . The aggregation or phase separation with a homogeneous distribution of aggregates is also seen in the three-dimensional images taken from films of thioPTCD/ClInPc (Figure 6c). Similar results were obtained for all the other PTCD/Pc mixed films that were fabricated. The point-to-point (steps of $1\text{ }\mu\text{m}$) generated images (parts b and d of Figure 6), where the full SERRS spectrum is recorded at each point on the film's surface, require long acquisition times. In parts b and d of Figure 6, the bright coloration is related to the relative intensity of the 1302 cm^{-1} vibration for bisPTCD and the 1393 cm^{-1} vibration for thioPTCD. The point-to-point maps confirm the results from wide field images showing that the structure of the mixed thin films is a distribution of aggregates from both materials. There is no evidence for molecular mixing in this particular set of mixed film experiments.

Conclusions

Mixed films have been formed by the co-evaporation of PTCD and Pc materials on glass and glass that is coated with silver islands. The Raman and surface-enhanced Raman spectra of mixed films of bisPTCD/Pc and thioPTCD/Pc have been investigated using laser lines in and out of resonance with the electronic absorption of the PTCD chromophore. The spectroscopic data permits one to conclude that the co-evaporated mixed films are formed by a random distribution of large aggregates of both materials and there is no evidence of molecular mixing. SERS allows one to obtain global images of the films using laser power as low as a 1 mW. Global images provide a powerful analytical technique to determine the degree of mixing or phase separation within micrometer spatial resolution.

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