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Spectroscopic characterization of thin solid films of a bis(chlorobenzylimidoperyleneimido)octane derivative†

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The synthesis, the fabrication of thin solid films and the spectroscopic characterization of a member of a new series of bis(perylene) materials, bis(chlorobenzylimidoperyleneimido)octane (BPTCDOc), are reported. The objective of the present work was to study the fabrication of submicron evaporated thin solid films of this high molecular mass perylene dye. The molecular organization of the vacuum evaporated nanometric films formed on dielectric substrates was probed using transmission infrared spectroscopy. Films fabricated on metallic surfaces were studied by reflection-absorption infrared spectroscopy (RAIRS). The fundamental vibrational modes were obtained from the FT-IR, FT-Raman and resonance Raman scattering (RRS) of isotropic solid samples. The vibrational assignment of characteristic wavenumbers is proposed. Surface-enhanced resonance Raman scattering (SERRS) allows the observation of vibrational fundamentals as well as combinations and overtones. The report includes the electronic absorption and emission spectra, extinction coefficients, monomer and excimer fluorescence.

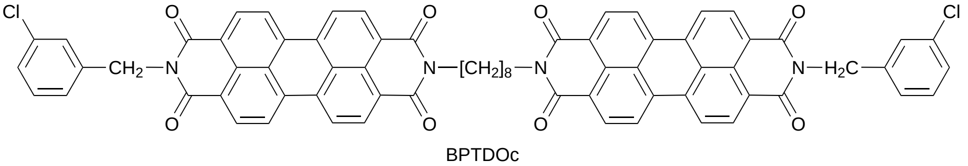
Perylene tetracarboxylic (PTC) derivatives are being intensively investigated due to their useful electroactive and photoactive properties with many potential applications in optoelectronics.[1] In particular, PTC materials are at the centre of a research effort intended to improve the n-type electron transporting-conduction properties by introducing chemical groups into the main PTC backbone.[2] Since in most applications the materials would be used in the form of ultrathin films, the fabrication and spectral characterization of submicron vacuum evaporated films is the main objective of our research efforts. Recently, we reported the film fabrication and spectral properties of the bis(chlorobenzylimidoperyleneimido)propane (BPTDPr) analogue of the BPTCDOc studied here. In BPTDPr, the two PTC groups are attached to the ends of a propane molecule.[3] The main conclusions from the BPTDPr work were that thin solid films can be prepared by vacuum evaporation. The films were anisotropic due to molecular organization. From the information provided by the transmission infrared spectra of films on dielectric substrates and RAIRS of films on smooth silver surfaces[4] it was gleaned that the molecular units are preferentially oriented face-onto the substrate. It was therefore of prime interest to determine the effect of the chain length (propane *versus* octane) of the bis(perylene) in the molecular organization and aggregation in the solid films.

Experimental

Preparation of BPTDOc

To a suspension of 2.27 g (0.0044 mol) of perylene-3,4,9,10-tetracarboxylic acid monoanhydride mono(3-chlorobenzyl)imide[5,6] in 75 ml of *N*-methylpyrrolidinone was added 0.288 g (0.20 mol) of 1,8-diaminooctane. The mixture was stirred at room temp. for 20 min then was heated to reflux (202 °C) for $2\frac{1}{2}$ h. The resultant black suspension was cooled to 150 °C then was filtered through a glass fibre filter (Whatman Grade GF/F) which had been preheated with boiling dimethylformamide (DMF). The solid was washed with 4 × 50 ml portions of boiling DMF. The initial filtrate was dark brown; the final boiling DMF filtrate was faint orange. The solid was washed with 25 ml of 2% aqueous potassium hydroxide followed by 2 × 25 ml portions of water and 3 × 25 ml portions of methanol. The product was dried at 60 °C to give 2.0 g (90% yield) of fine black solid; mp 476 °C (Calc. for $C_{70}H_{44}N_4Cl_2O_8$: C 73.75, H 3.89, N 4.91; found: C 72.61, H 3.74, N 4.79%). The pigment was insoluble in common NMR solvents; a spectrum in concentrated D_2SO_4, although it gave broad peaks, was consistent with the proposed structure: δ_H (300 MHz, D_2SO_4, internal $SiMe_4$) 8.7 (m, 16H, perylene ring protons), 7.02 (s, 2H, chlorophenyl), 6.99–6.90 (m, 6H, chlorophenyl), 5.20 (br s, 2H, N-CH_2 benzyl), 4.06 (br, 4H, N-CH_2 octyl), 1.50, 1.12, 1.05 (br s, 24H, internal octyl methylenes).

BPTDOc films were deposited onto a variety of substrates: glass slides for visible absorption and fluorescence work, polished KBr discs for transmission FT-IR and 100 nm mass thickness of silver on glass for reflection-absorption infrared spectroscopy. Silver islands, 6 nm mass thickness, were used for SERRS experiments. The silver films were prepared under high vacuum (10^{-6} mbar) by thermal evaporation onto glass slides held at 200 °C. Film thickness was monitored by an XTC Inficon quartz crystal oscillator. The solutions of the dye were prepared using a mixed solvent containing 10% trifluoroacetic acid (spectroscopic grade, Aldrich) in CH_2Cl_2. The absorption spectra were recorded using a Response single beam spectrometer interfaced to an IBM microcomputer. The fluorescence and Raman spectra were recorded using the 514.5 nm line of the Ar^+ laser as an excitation source and both a THR 1000 spectrograph with a liquid nitrogen cooled



BPTDOc

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† IUPAC name: 1,8-Bis{9-(3-chlorobenzyl)-1,2,3,8,9,10-hexahydro-1,3,8,10-tetraoxoisoquino[6′,5′,4′:10,5,6]anthro[2,1,9-*def*]isoquinolin-2-yl}octane.

CCD detector and a Ramanor U1000 double monochromator spectrometer. All spectra were recorded in a back-scattering geometry using a microscope attachment and a × 100 objective and a 4 cm^{-1} resolution. SERRS spectra were also recorded using the 633 nm laser line in the Renishaw system 2000 with 2 cm^{-1} resolution. The infrared spectra were recorded with 1 cm^{-1} resolution using a Bomem DA3 FTIR equipped with a liquid nitrogen cooled MCT detector. The reflection-absorption infrared spectra were recorded on an in-house modified Bomem 110-E equipped with a Judson mid-range (650 cm^{-1}) 1 × 1 mm MCT detector.[7,8] Annealing of the sample during the RAIRS measurements was performed *in situ* on the heating plate. The FT-Raman spectra were measured on Bruker RFS 100 stand-alone spectrometer.

Results and Discussion

Electronic spectra

The absorption spectra of PTC derivatives have been recently calculated and assigned.[9,10] The observed visible absorption spectrum consists of one electronic transition with the corresponding vibronic structure. The absorption spectrum of BPTDOc shows the characteristic vibronic structure associated with the π–π* transition of the perylene moiety, with a 0–0 band at 538 nm. A concentration dependent broad band at 598 nm, probably due to aggregation in solution, and a second electronic transition at 376 nm were also seen in the spectrum. The extinction coefficients (ε) obtained from the absorbance *vs.* concentration measurements in solution are shown below.

band centre/nm	ε/l mol^{-1} cm^{-1}
376	9.0×10^3
470	2.68×10^4
501	3.01×10^4
538	3.49×10^4
598	2.22×10^4

The fluorescence spectra of the same solutions yielded a mirror image of the absorption spectrum with maxima at 540, 577 and a weak band at 635 nm. The absorption spectrum of the neat solid in a KBr dispersion shows band broadening with maxima close to the monomer absorption. The emission obtained with 514.5 nm excitation is typical of an excimer emitter with a maximum at 665 nm as can be seen in Fig. 1; intensity units are arbitrary. The absorption and emission spectra of a 25 nm film of BPTDOc are also shown in Fig. 1. The absorption spectrum is similar to that of the pellet, and so is the emission spectrum obtained with 514.5 nm excitation. It can be concluded that in the solid samples the main emitters are excimers. The effect of molecular orientation and intermolecular interactions on the electronic band broadening of ultrathin organic films has been discussed.[11] In the latter report, it was confirmed that the orientational distribution has a significant effect on the spectral profile (bandwidth and symmetry). In general, thin film structure information may also be extracted using vibrational properties (from IR and Raman) such as band positions, band halfwidth and band relative intensities.

FT-Raman, resonant Raman and surface-enhanced resonant Raman scattering

The off-resonance FT-Raman spectra of the bulk in a KBr pellet and the resonant Raman scattering (RRS) spectra of the 25 nm film are presented in Table 1. The SERRS spectrum of a 10 nm evaporated film on silver islands obtained with the 633 nm laser line is presented in Fig. 2. Both the spontaneous and resonant Raman spectra are determined by the vibrational modes of the PTC chromophore. The characteristic vibrational modes of the perylene moiety are observed in the FT-Raman spectrum at 1297, 1377, 1573 and 1586 cm^{-1}.[12,13] The symmetric carbonyl stretching is also seen at 1695 cm^{-1}. The

Table 1 BPTDOc-observed Raman wavenumbers, relative intensities and full width at half maximum (FWHM) in cm^{-1}

FT-Raman-FWHM	RRS-FWHM	SERRS-FWHM	assignment
		265 (11) 24	per. deformation
542 (20) 15	545 (25) 13	539 (5) 11	per. deformation
		556 (36) 14	per. deformation
		588 (9) 16	alkyl deformation
		931 (3) 8	per. deformation
		1041 (2) 7	C—H$_2$ bend
		1068 (10) 16	C—H bend
1083 (14) 16	1087 (9) 13	1085 (3) 8	C—H bend
		1243 (18) 16	C—H$_2$ bend
		1263 (20) 19	C—H$_2$ bend
		1276 (24) 11	C—H$_2$ bend
		1286 (37) 7	C—H$_2$ bend
1297 (100) 24	1295 (70) 12	1293 (100) 16	C—H bend + ring st.
	1306 (93) 13	1306 (46) 24	per. ring st.
		1326 (24) 8	C—H$_2$ bend
		1350 (43) 7	C—N stretch
		1357 (49) 21	C—N stretch
1377 (95) 19	1381 (100) 13	1377 (90) 16	per. ring st.
		1387 (31) 14	per. ring st.
1456 (19) 15	1459 (24) 10	1455 (11) 21	per. ring st.
		1477 (14) 11	per. ring st
		1539 (10) 23	per. ring st.
		1568 (13) 5	C=C stretch
1573 (77) 20	1575 (14) 10	1573 (68) 18	C=C stretch
1586 (80) 18	1589 (77) 15	1586 (22) 25	C=C stretch
	1615 sh	1612 (14) 14	C=C stretch
		1650 (11) 8	C=O stretch
1695 (21) 16		1674 (7) 21	C=O stretch

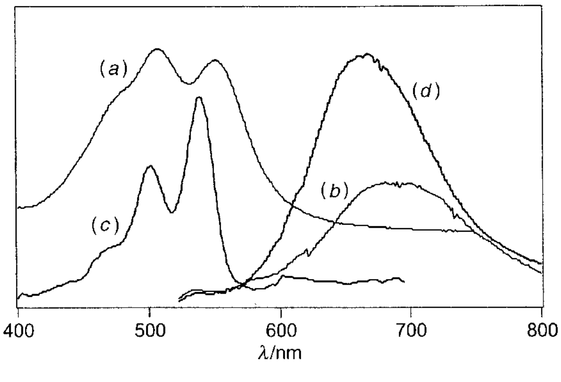

Fig. 1 Absorption (*a*) and emission (*b*) spectra of a 25 nm BPTCDOc film. The absorption of a dilute solution (*c*) and the fluorescence of the BPTCDOc pellet (*d*) are also shown. Excitation at 514.5 nm.

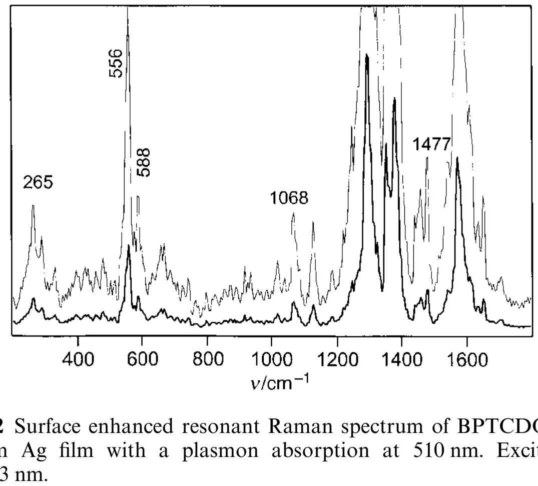

Fig. 2 Surface enhanced resonant Raman spectrum of BPTCDOc on 10 nm Ag film with a plasmon absorption at 510 nm. Excitation at 633 nm.

$1297\ \mathrm{cm^{-1}}$ band in the FT-Raman spectrum has a large FWHM (full width at half maximum) value of $24\ \mathrm{cm^{-1}}$. Deconvolution of the band shows the presence of at least two components: the higher wavenumber component is prominent in the RRS spectra of the pellet and that of the thin solid film at $1306\ \mathrm{cm^{-1}}$, while the lower wavenumber ($1293\ \mathrm{cm^{-1}}$) is prominent in the SERRS spectrum. Notably, the SERRS spectrum is not simply the amplified version of the RRS spectrum. Both spectra are mainly due to the PTC moiety, however the relative intensities in the $1293–1306\ \mathrm{cm^{-1}}$ and the $1573–1586\ \mathrm{cm^{-1}}$ pairs are different. The differences between SERRS and RRS are identified as relative SERRS intensity changes of the same normal modes present in the RRS and in the FT-Raman spectra. The FT-Raman and the RRS spectra are due to inelastic scattering from aggregates in the solid samples and films. The SERRS spectrum is obtained from the molecular layers coating the metal surface and the relative intensity of active modes is modulated by the orientation of the adsorbate on the metal surface. From the observed wavenumbers (RRS *vs.* SERRS) it was deduced that the BPTDOc molecules are physisorbed onto the surface of the silver islands. The FWHM values of Raman bands vary considerably as can be seen in Table 1. The explanation may be found in band overlapping since the two PTC moieties generate vibrational modes having nearly degenerate wavenumbers. The RRS and SERRS spectra show the fundamental, combinations and overtones characteristic of the PTC chromophore.[14] Notably, the overtones and combinations are not detected in the FT-Raman spectrum. The SERRS relative intensity of combinations and overtones shows dramatic changes when the exciting laser line is switched from 488 or 514.5 to 633 nm as illustrated in Fig. 3. Observing overtones and combination band progressions in this large organic molecule is in itself a fact worthy of an independent study to interpret the intensities in terms of ground and excited state potential surfaces. Such a study is in progress for a series of perylene derivatives. Qualitatively, the perylene modes which have the largest displacements would have the largest overtone intensities, and overtones for high frequency bands are more intense than those of low frequency bands.[15] In summary, the spontaneous Raman, the RRS and the SERRS spectra of the bis(perylene) molecule are not very different from those of the single perylene tetracarboxylic derivatives. A complete listing of the observed wavenumbers in SERRS, relative intensities determined from peak areas, and their FWHM values are also given in Table 1.

Infrared spectra

The observed infrared wavenumbers for the isotropic dispersion of BPTDOc in KBr, the 25 nm evaporated film and RAIRS of a 25 nm film on silver are given in Table 2. For examination of molecular organization in the vacuum evaporated films it is reasonable to limit the discussion of normal mode assignment to the characteristic in-plane and out-of-plane vibrations of the chromophore moiety. The most relevant in-plane molecular vibrations of the PTC group are as follows. (i) The two strong carbonyl stretching vibrations: the antisymmetric stretching at $1662\ \mathrm{cm^{-1}}$ and symmetric C=O stretching at $1696\ \mathrm{cm^{-1}}$. Notably, the symmetric C=O vibration is also seen in the Raman spectrum, supporting the local symmetry assignment for this mode. (ii) The strongest in-plane perylene C=C stretching vibrations are observed at 1595 and $1578\ \mathrm{cm^{-1}}$.[12,13] (iii) The out-of-plane wagging vibrations of the perylene ring have a dynamic dipole perpendicular to the perylene plane and also perpendicular to those of the carbonyl or C=C stretching vibrations. The out-of-plane modes are observed with characteristic wavenumbers at 810 and $748\ \mathrm{cm^{-1}}$ corresponding to the C—H wagging vibrations. These out-of-plane modes are normally observed with high relative intensity as can be seen in Fig. 4. The assignment of the in-plane and out-of-plane modes of the perylene moiety allows one to elucidate the molecular orientation of the chromophore in the evaporated film.

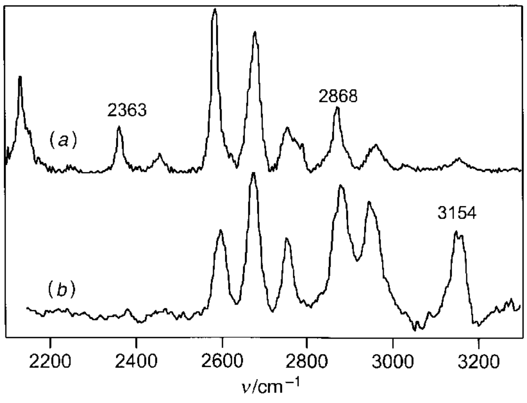

Fig. 3 Combinations and overtones in the SERRS spectra of BPTCDOc obtained with excitation at (*a*) 633 and (*b*) 514.5 nm

Molecular organization

The molecular orientation creates a film anisotropy that can be extracted using the change in relative intensity observed in the spectra recorded in the transmission geometry for the isotropic sample and the film as shown in Fig. 4. In the transmission geometry, the polarization of the incident radiation always lies along the substrate surface (parallel to the surface). The KBr pellet spectrum is the reference with random spatial distribution of monomer and aggregates. In a vacuum evaporated film, the molecular vibrational modes that generate a change in dipole moment parallel to the substrate surface will be intense in the infrared spectrum. Fundamental vibrational modes corresponding to a change in dipole moment perpendicular to the substrate surface will not absorb. It can be seen in the transmission spectrum of the film that the wagging bands are very weak, while the in-plane vibrations remain strong. Since the intensity is proportional to the dot product of the electric field and the dynamic dipole, in average, the PTC plane should be parallel to the substrate surface.

The reflection-absorption spectra are commonly used to extract information about molecular orientation on smooth reflecting surfaces.[16] In this case, the reflecting surface polarizes the light perpendicular to the surface plane. Therefore, the intensity of vibrational modes with a dynamic dipole perpendicular to the surface are enhanced and those modes with a dynamic dipole parallel to the surface are suppressed. The reflection-absorption spectra of a BPTCDOc film on silver are given in Fig. 5. The series of spectra correspond to an organic films that underwent post-deposition annealing at 50, 100, 150 and 200 °C. The wagging vibrations at 810 and $748\ \mathrm{cm^{-1}}$ remain intense in all the RAIRS spectra shown in Fig. 5. In fact, their relative intensity has increased in comparison to the in-plane modes. It can be concluded that the evaporated film on smooth silver, on average, also has molecular oganization where the PTC plane is close to being parallel to the substrate surface. The spectra shown in Fig. 5 also indicate that the film structure is not strongly modified by annealing. However, the relative intensity of the out-of-plane modes does show a slight decrease in intensity with increasing temperature (see spectrum at 200 °C), an indication that film organization is lost at elevated temperatures. In summary, vacuum evaporated films onto KBr have molecular organization where the PTC moieties are oriented parallel to the substrate surface. Similarly, BPTDOc films formed onto a smooth silver surface also show a certain degree of organization with the perylene groups in a nearly face-on orientation. Finally, it should be pointed out that the film anisotropy is solely observed in the direction

Table 2 BPTDOc observed IR wavenumbers, relative intensities (I) and full width at half maximum (FWHM) in cm^{-1}

pellet			film			RAIRS			100 °C			200 °C			
I/cm^{-1}	I	FWHM/cm^{-1}	I/cm^{-1}	I	FWHM/cm^{-1}	I/cm^{-1}	I	FWHM/cm^{-1}	I/cm^{-1}	I	FWHM/cm^{-1}	I/cm^{-1}	I	FWHM/cm^{-1}	assignment
748	40	*6*	749	4	*5*	749	44	*13*	749	47	*13*	749	55	*8*	per. wag
			784	7	*14*	784	11	*14*							alkyl wag
794	10	*9*	794	10	*8*	794	22	*12*	794	4	*7*	794	6	*10*	alkyl wag
810	52	*5*	810	16	*6*	811	100	*6*	811	100	*6*	811	71	*6*	per. wag
854	8	*17*				854	35	*27*	855	22	*16*	854	16	*13*	per. wag
1173	7	*7*	1173	4	*8*	1173	15	*17*	1173	6	*9*	1173	10	*12*	C—H bend
1275	3	*10*	1275	23	*10*	1276	9	*16*	1276	15	*23*	1276	12	*20*	C—H_2 bend
1340	63	*21*	1339	31	*11*	1341	43	*22*	1341	40	*23*	1341	40	*28*	C—N stretch
1362	10	*11*	1362	22	*13*	1365	16	*10*	1362	24	*19*	1362	50	*14*	C—N stretch
1403	44	*6*	1401	16	*8*	1402	11	*7*	1402	14	*7*	1402	32	*7*	per ring str.
1440	28	*11*	1435	16	*10*	1436	16	*11*	1436	21	*19*	1436	32	*17*	CH_2 scissors
1475	5	*10*	1475	6	*6*	1474	10	*11*	1474	6	*19*	1474	16	*17*	per ring str.
1578	31	*10*	1577	26	*10*	1577	19	*11*	1577	17	*19*	1577	21	*13*	C=C ring str
1595	89	*9*	1594	71	*10*	1595	48	*11*	1595	45	*12*	1594	90	*11*	C=C ring str
1654	54	*17*	1656	68	*14*	1653	36	*15*	1654	8	*14*	1654	14	*17*	C=O str
1662	58	*13*	1662	41	*10*	1663	64	*16*	1661	55	*17*	1660	63	*13*	C=O str
						1682	48	*22*	1681	15	*12*	1680	12	*12*	C=O str
1696	100	*14*	1695	100	*21*	1698	79	*14*	1698	71	*23*	1697	100	*16*	C=O str

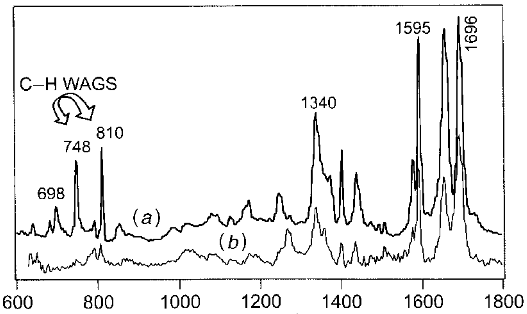

Fig. 4 Infrared spectra of BPTCDOc: (*a*) isotropically dispersed sample and (*b*) 25 nm film on KBr

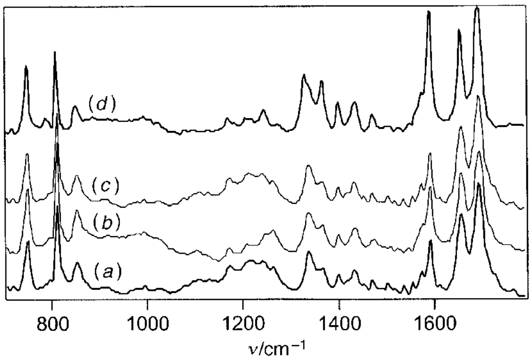

Fig. 5 Reflection absorption spectra of BPTCDOc on smooth silver surface and RAIRS after post-deposition annealing at (*a*) 50, (*b*) 100, (*c*) 150 and (*d*) 200 °C

perpendicular to the plane of the substrate. Infrared transmission measurements with polarized light indicated that there is no anisotropy in the plane of the substrate.

Conclusion

A member of a new class of perylene derivatives, 1,8-bis(3-chlorobenzylimidoperyleneimido)octane, is reported and characterized by optical spectroscopy. It has been demonstrated that thin solid films of this materials can be fabricated by vacuum evaporation. The molecular organization in these films was extracted using infrared polarization spectroscopy. BPTDOc molecules to a large degree aligned themselves in the film with the perylene chromophore face-on to the substrate. This alignment is observed independently on dielectric and metal surfaces. Some of the alignment is lost by post deposition annealing above 200 °C. Observed vibrational modes are assigned. All the Raman spectra are characteristic of the perylene tetracarboxylic chromophore.

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References

1 J. F. Lam, S. R. Forrest and G. L.Tangonan, *Phys. Rev. Lett.*, 1991, **66**, 1614.
2 G. Horowitz, F. Kouki, P. Spearman, D. Fichou, C. Nogues, X. Pan and F. Garnier, *Adv. Mater.*, 1996, **8**, 242.
3 S. Rodriguez-Llorente, R. Aroca, J. Duff and J. A. DeSaja, *Thin Solid Films*, in press.
4 E. Johnson and R. Aroca, *Appl. Spectrosc.*, 1995, **49**, 472.
5 H. Troster, *Dyes and Pigments*, 1983, **4**, 171.
6 E. Spietschka and H. Troster, *US Pat.* 4 709 029, November 1987.
7 C. P. Tripp and M. L. Hair, *Appl. Spectrosc.*, 1992, **46**, 100.
8 D. A. Guzonns, M. L. Hair and C. P. Tripp, in *Fourier Transform Infrared Spectroscopy in Colloid & Interface Science*, ed. D. R. Scheuing, 1990, p. 237.
9 R. Mercadante, M. Trsic, J. Duff and R. Aroca, *J. Mol. Struc., Theochem*, 1997, **394**, 215.
10 M. Adachi, Y. Murata and S. Nakamura, *J. Phys. Chem.*, 1995, **99**, 14 240.
11 C. E. Evans, Q. Song and P. W. Bohn, *J. Phys. Chem.*, 1993, **97**, 12 302.
12 R. Aroca, A. K. Maiti and Y. Nagao, *J. Raman Spectrosc.*, 1993, **24**, 227.
13 A. K. Maiti, R. Aroca and Y. Nagao, *J. Raman Spectrosc.*,1993, **24**, 351.
14 R. Aroca and R. E. Clavijo, *Spectrochim. Acta*, *Part A*, 1991, **47**, 271.
15 J. I Zink and K. S. K. Shin, in *Advances in Photochemistry*, ed. D. H. Volman, G. S. Hammond and D. C. Necker, 1991, **16**, pp. 119–213.
16 B. E. Hayden, in *Vibrational Spectroscopy of Molecules on Surfaces, Methods of Surface Charaterization*, ed. J. T. Yates and T. E. Madey, Plenum Press, New York, 1987, p. 267.

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