the conversion of these high-oxygen polymers to low-oxygen silicon carbide ceramics were obtained by analyzing the pyrolysis products by elemental analysis, quantitative X-ray diffraction, ^{29}Si MAS NMR spectroscopy, Raman spectroscopy, and transmission electron microscopy. We have found that the pyrolysis proceeds by the formation of an amorphous SiCO material at 1200 °C, that is composed of all possible SiCO coordination tetrahedra. Surprisingly this ceramic material is compositionally stable to ~1500 °C. At 1400 °C this material has structurally undergone a Si–O for Si–C redistribution into SiC_4 and SiO_4 as the silicon environments. The carbon not bound to the silicon is present as small (~5 nm) discrete domains of graphite. After pyrolysis to 1600 °C the ceramic loses ~80% of the oxygen present at 1200 °C and is composed predominantly of crystalline β-SiC with only traces of SiO_4. The excess carbon present is similar to a glassy carbon with ~35-Å domain size. The lack of any evidence for mixed SiCO species at these temperatures supports a vapor-phase carbothermic reduction mechanism as described in Scheme II, with SiO and CO_2 as the key intermediates. At 1800 °C the pyrolysis is complete, and the final ceramic is composed of substantial amounts of SiC with many of the SiC crystallites twinned. The carbon is a disordered diamond type of carbon with a ~50-Å domain size and a structure typical of turbostratic graphite.

Acknowledgment. The authors thank Dow Corning Corp. for the support of this work and Dr. Ann Leugers of the Dow Chemical Co. for her assistance with the Raman spectroscopy. Microstructural analysis was done at the Center for Microanalysis of Materials of the Materials Research Laboratory, UIUC, which is supported by the U.S. Department of Energy under Contract DE-FG02-91ER45439.

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Spectroscopic Characterization of Rare-Earth Octa-*tert*-butylbisphthalocyanine Complexes

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The spectroscopic characterization of rare-earth octa-*tert*-butylbisphthalocyanine (R_8Pc_2Ln or $LnPc^t_2$) complexes is reported. Surface-enhanced resonance Raman of Langmuir–Blodgett films on Au island films, infrared of solids and UV–visible spectra of solid films and solutions were recorded. Complementary spectroscopy data on ultrathin solid films of rare-earth-unsubstituted bisphthalocyanines ($LnPc_2$) were also obtained. The complexes that were studied were the blue and the green materials of lanthanide (Ln) elements that were obtained by direct synthesis. The green material previously assigned to the stable free radical in the $LnPc_2$ series, gave characteristic electronic, infrared, and resonant Raman spectra for the entire $LnPc^t_2$ series. The blue material $LnHPc^t_2$ (and $LnHPc_2$) produced infrared, Raman, and electronic spectra that could be associated with the presence of two Pc^{2-} ligands. The spectral properties of the blue form were similar to that of $ZrPc_2$ where the central atom Zr(IV) is attached to two Pc^{2-} ligands. The synthesis of lanthanide mono and bisphthalocyanines are also described.

Introduction

The changes in the optical spectra of liquids and solids by the presence of an external electric field was referred to as the "electrochromic" effect. The term was introduced by Platt[1] for an effect that was mostly observed in aromatic compounds.[2] The electrochromic effect is commonly invoked to describe the faradaic electrochemical reaction that results in a color change of a material deposited on the surface of an electrode.[3,4] The electrochromic properties of rare-earth element (REE) bisphthalocyanines have stimulated a thorough investigation of these compounds.[5] The materials could also find potential applications in such areas as gas sensors and molecular electronics.[6,7]

Metal-free phthalocyanine H_2Pc and metalated phthalocyanine MPc that are composed of a single Pc ligand are blue. Their absorption spectra are dominated by a Soret and a Q band. However, transition-metal complexes consisting of a single Pc ligand may show an additional absorption band in the 500-nm region (assigned to a charge-transfer transition), and they appear green. An extensive discussion on the electronic properties of Pc molecules can be found in a recent review by Stillman and Nyokong.[7] Mono Pc of rare-earth metals (i.e., $LnPc^tX$, Pc^t = tetra-*tert*-butylphthalocyanine, X = anion)[8] are also characterized by a simple absorption spectrum without the charge-transfer band in the 500-nm region. The one-electron oxidation product of $LnPc^tX$, however, contained an absorption band in the 500-nm region. Under mild oxidative conditions, the oxidation of the Ln^{3+} cation can be ruled out, and the observed absorption band near 500

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nm could be assigned to the phthalocyanine radical ($Pc^{\bullet -}$) anion. The assignment is also consistent with the reported radical anion found in PcLi.[9] Chemical or electrochemical reduction of the radical anion leads to the disappearance of the visible band in the 500-nm region. Similar results were also reported in the $LnPc_2$ (Ln = Dy, Tm, Yb, Lu) series where chemical reduction led to the disappearance of the near-infrared band which was associated with the radical anion.[9] The near-infrared absorption band was assigned to $Pc^{2-} \rightarrow Pc^{-}$ intramolecular charge-transfer transition.[10] Clarisse and Riou[11] reported that the green bisphthalocyanine complex of Lu was consistent with the $LuPc_2$ formula, based on their elemental analysis. The free-radical nature of the green material of $LuPc_2$ ($Pc^{2-}LnPc^{\bullet -}$) has thereby been well established. Direct synthesis of rare-earth bisphthalocyanine complexes may also lead to a neutral blue product that has the general formula $LnHPc_2$ as speculated in the early work of Kirin et al.[12] It should be noticed that the blue product observed in electrochemical experiments of lanthanide bisphthalocyanine corresponds to $[Pc^{2-}Ln^{3+}Pc^{2-}]^{-}$ anion. Moussavi et al.[13] have published the crystal and UV–vis spectroscopic data for green and blue materials of lutetium bisphthalocyanine. They confirmed that $LuPc_2$ was the formula of the green product and proposed that $LuHPc_2$ was the molecular formula of the blue material. They however pointed out that the extra hydrogen or "acidic hydrogen" in the blue form could not be located by X-rays. Similarly, Kasuga et al.[14] have reported the structural formulas $NdPc_2$ and $NdHPc_2$ to describe the green and the blue materials respectively of neodymium bisphthalocyanine complexes.

Our interests in rare-earth complexes of phthalocyanine is in the potential use of these molecules mostly as ultrathin solid films and Langmuir–Blodgett (LB) monolayers. In the present work, the $LnPc^{t}_{2}$ (green) and $LnHPc^{t}_{2}$ or [$LnPc^{t}_{2}$ (blue)] materials for all stable REE were studied using visible, infrared, and surface-enhanced Raman spectroscopy. The optical signatures of the green and blue materials of $LnPc^{t}_{2}$ complexes were used to identify the contamination products present in sublimed thin films of the early lanthanide bisphthalocyanine complexes.

Experimental Section

The synthesis of stable green and blue materials of octa-*tert*-butylbisphthalocyanine of lanthanide elements has been previously reported.[15,16] Lanthanide phthalocyanine derivatives are formed by heating a 8:1 mole ratio of 4-*tert*-butylphthalonitrile and lanthanide salt (LnX_3) to ca. 290 °C. The first step in the formation of the bisphthalocyanine is the generation of the lanthanide monophthalocyanine complex ($LnPc^{t}X$). Early rare-earth elements (REE) form the $LnPc^{t}X$ complex after 5–10 min, and heavier REE require 1–1.5 h. Prolonged heating is used to convert $LnPc^{t}X \rightarrow LnPc^{t}_{2}$ (green product) and $LnPc^{t}_{2}$ (green material) $\rightarrow LnHPc^{t}_{2}$ (blue product). The green form of europium bisphthalocyanine could not be isolated due to the rapid conversion to the blue material. The rate of green → blue bisphthalocyanine conversion was dependent on the REE and the temperature. For instance, 3 h of heating at 290 °C was sufficient to produce $LnHPc^{t}_{2}$ (Ln = Gd, Tb, Ho, Er, Tm, Yb). The blue product of lutetium bisphthalocyanine, however, required 6–8 h of heating at 300–310 °C. The electronic absorption spectra of $DyPc^{t}Cl$, $DyPc^{t}_{2}$, and $DyHPc^{t}_{2}$ are shown in Figure 1 to illustrate the differences between lanthanide mono- and bisphthalocyanine complexes. The electronic spectra of $DyPc^{t}X$ contained a Soret band at 330 nm and a Q band at 674 nm. The position of the Q band in lanthanide monophthalocyanine complexes was independent on the Ln element, and the "free radical band" at ca. 450 nm was not observed.

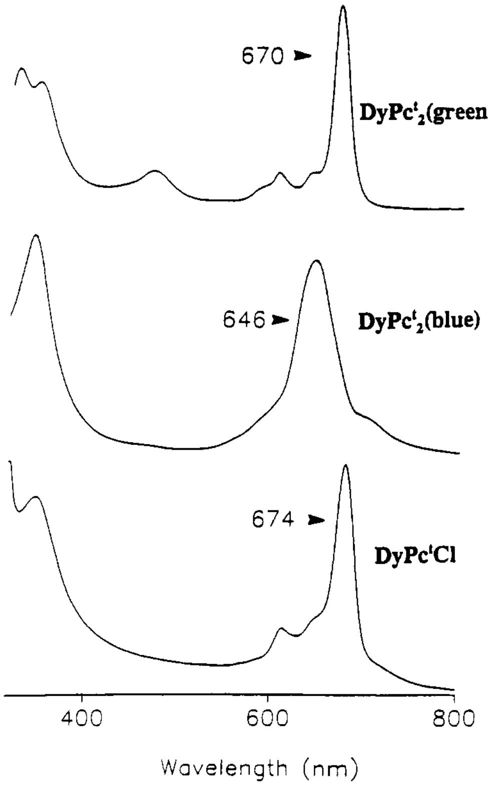

Figure 1. Electronic absorption spectra of the $DyPc^{t}_{2}$ (green), $DyHPc^{t}_{2}$ (blue), and $DyPc^{t}Cl$ materials in toluene solution.

The detailed synthesis of the green form of lutetium octa-4-*tert*-butylbisphthalocyanine are given here as a typical example. In a glass tube were placed 2.94 g of 4-*tert*-butylphthalonitrile and 0.62 g of lutetium formate. The tube was evacuated and heated gradually to 290 °C. After ca. 1.5 h of heating at 290 °C a green product was formed. Purification of $LuPc^{t}_{2}$ was carried out on an aluminum oxide column using benzene as the solvent. The solvent was removed with vacuum (655 Pa) and heat (150 °C). The product was 2.31 g (70% yield) of $LuPc^{t}_{2}$($C_{96}H_{96}LuN_{16}$). The structure was confirmed by elemental analysis (found: C 70.33%, H 5.98%, N 12.92%; calcd: C 69.96%, H 5.82%, N 12.97%). The blue material of lutetium octa-4-*tert*-butylbisphthalocyanine was formed by prolonged heating of the green material. Elemental analysis of the blue form also support an octa-*tert*-butyllanthanide bisphthalocyanine complex. Table I lists the electronic absorptions of $LnPc^{t}_{2}$ and $LnHPc^{t}_{2}$ materials recorded in toluene solutions. The materials were isolated on TLC sheets (silica gel 60) and purified on a aluminum oxide column using benzene as the solvent.

The synthesis of the green and blue materials of unsubstituted bisphthalocyanines ($LnPc_2$) is similar to $LnPc^{t}_{2}$ but requires more severe conditions. For example, the reaction mixture involving Ce, Nd, and Sm, requires heating at 300–310 °C for 3–5 h to yield the blue $LnHPc_2$ material. The synthesis of the blue $LuHPc_2$ material requires about 12 h of heating.

Thin films (ca. 200 nm) of the green form of $LnPc_2$ were sublimed to a Corning 7059 substrate and halide crystals. The pressure in the evaporator during film deposition was 5×10^{-3}

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Table I. Observed Absorptions (nm) in the Electronic Absorption Spectra of Lanthanide Bisphthalocyanine Materials in Toluene Solutions[a]

Ln	green material	blue material
Ce		335 (0.85), 645 (1.00)
Pr	326 (1.00), 351 (0.65), 487 (0.24), 614 (0.36), 686 (0.92)	342 (0.89), 649 (1.00)
Nd	327 (1.00), 351 (0.68), 470 (0.22), 607 (0.34), 675 (0.93)	342 (0.86), 648 (1.00)
Sm	327 (0.97), 344 (0.84), 476 (0.22), 612 (0.33), 652 (0.41), 678 (1.00)	342 (0.91), 648 (1.00)
Eu	326 (1.00), 342 (0.91), 471 (0.28), 611 (0.40), 645 (0.56), 675 (1.00)	342 (0.94), 647 (1.00)
Gd	325 (0.83), 345 (0.67), 469 (0.21), 607 (0.27), 645 (0.24), 674 (1.00)	340 (1.00), 647 (0.97)
Tb	325 (0.80), 340 (0.71), 468 (0.20), 606 (0.26), 645 (0.35), 671 (1.00)	342 (1.00), 647 (0.95)
Dy	324 (0.85), 340 (0.80), 466 (0.21), 605 (0.27), 644 (0.42), 670 (1.00)	342 (1.00), 646 (0.93)
Ho	322 (0.85), 341 (0.73), 466 (0.26), 604 (0.30), 642 (0.36), 668 (1.00)	342 (1.00), 642 (0.91), 703 (0.26)
Er	321 (0.76), 343 (0.64), 465 (0.24), 603 (0.24), 641 (0.21), 667 (1.00)	342 (1.00), 638 (0.88), 712 (0.18)
Tm	322 (0.70), 344 (0.63), 465 (0.19), 601 (0.20), 639 (0.25), 666 (1.00)	342 (1.00), 637 (0.92), 713 (0.19)
Yb	322 (0.74), 344 (0.60), 465 (0.22), 604 (0.21), 644 (0.17), 666 (1.00)	342 (1.00), 637 (0.90), 716 (0.18)
Lu	322 (0.68), 344 (0.60), 466 (0.20), 602 (0.18), 638 (0.17), 667 (1.00)	342 (1.00), 636 (0.96), 722 (0.18)

[a] Numbers in parenthesis are relative intensities.

Pa and the films were grown at a rate of 0.5–0.1 nm s^{-1} as measured by an Inficon XTC standard sensor and rate monitor. SERS-active substrates were prepared in an evaporator dedicated for metal film deposition. Four nm of Au or Ag was evaporated at a rate of 0.1 nm s^{-1} onto a glass substrate maintained at 220 °C. The plasmon resonance of the Ag and Au island film was centered at 505 and 607 nm, respectively.

Langmuir–Blodgett monolayers of $LnPc_2$ and $LnHPc^{t}_{2}$ were prepared and transferred to Corning 7059 glass slides and SERS substrates. The Corning glass substrates were cleaned by standing for 3 h in warm (90 °C) chromosulfuric acid. These slides were then rinsed and treated with NaOH (pH 11) for 12 h. All monolayer work was conducted on a Lauda Langmuir film balance equipped with an electronically controlled Lauda Filmlift FL-1 dipping device. The subphase consisted of water that was double distilled and passed through Milli-Q Plus filtration. The Ph of the subphase was recorded 5.5 prior to spreading the Pc derivatives from benzene solution. The Langmuir layer was compressed to 15 mN/m and transferred to the solid supports at a rate 4.8 mm/min.

A Spectra Physics Model 2020 Kr$^+$ ion laser operating at 647.1 or 676.4 nm and the 514.5-nm laser line of a Spectra Physics Model 164 Ar$^+$ were used for Raman excitation. Typical spectral bandpass and laser power were 4 cm^{-1} and 50 mW, respectively. Raman shifts were measured with a Spex-1403 double spectrometer. Infrared spectra were measured in BOMEM DA3 FTIR spectrometer. Electronic absorption spectra were recorded on a Response UV–vis spectrophotometer. For data analysis, all files were imported to Spectra Calc software available from Galactic Industries Corp. EPR measurements of solid samples were performed with a Bruker ESP 300E (equipped with frequency counter and precise Gauss meter) spectrometer at the X frequency.

Results and Discussion

Electronic Spectra. In the visible spectral region, the electronic absorption spectra of the blue and the green materials of the bisphthalocyanine complexes revealed very distinct patterns as shown in Figures 1 and 2. The green free-radical material presented a Soret band at 320 nm with a shoulder near 340 nm, a Q band near 670 nm, and a typical radical Pc anion band in the 460–490-nm region. A bathochromic shift in the Q absorption band (667 nm in $LuPc^{t}_{2}$, 686 nm in $PrPc^{t}_{2}$) was observed with the increase in the ionic radius of the REE. The free-radical nature of the green materials was confirmed by the EPR spectra, where a g value of 2.006 was observed for $HoPc^{t}_{2}$ and $TbPc^{t}_{2}$.

Corker et al.[4] characterized the green form of $LuPc_2$ and the electrochemically generated blue form. They reported an EPR-active green form and an EPR-silent blue form whose visible absorption spectra agree well with the data presented in Figures 1 and 2. An intramolecular charge transfer with free electron hopping between the two Pc rings was suggested in the green form of $LuPc_2$.[4] This model was later corroborated by Simon et al.[9,10]

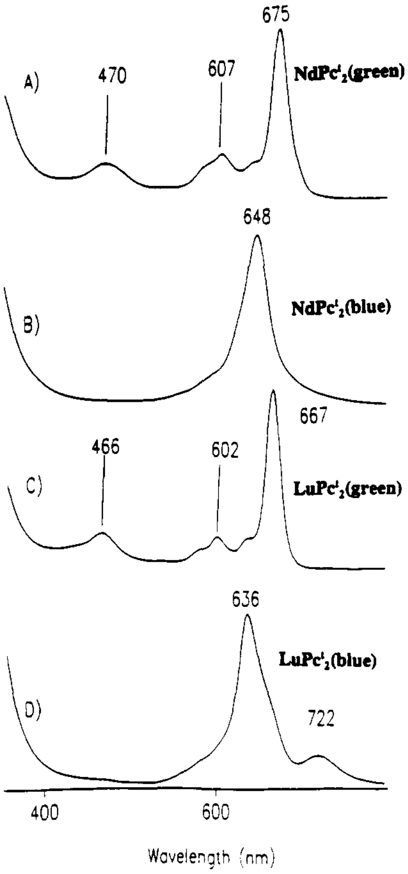

Figure 2. Electronic absorption spectra of the green (A) and blue (B) materials of $NdPc^{t}_{2}$ and green (C) and blue (D) materials of $LuPc^{t}_{2}$.

The electronic spectra of $LnHPc^{t}_{2}$ or blue materials were also similar to the spectra of bisphthalocyanine complexes that contain two Pc^{2-} ligands such as hafnium(IV) bisphthalocyanine,[17] zirconium(IV), bisphthalocyanine,[17] and uranium(IV) bisphthalocyanine.[18] $LnHPc^{t}_{2}$ (blue products) have a broad and blue shifted Q-band (ca. 640 nm) with respect to the Q-band in $LnPc^{t}_{2}$ (green). A weak satellite of the Q-band was observed at 700 nm in the spectra of $LnHPc^{t}_{2}$ (Ln = Er, Tm, Yb, Lu). This band appeared as a shoulder in Ho, Dy, Tb, and Gd blue complexes, and it was completely absent in the spectra of Eu, Sm, Nd, and Pr complexes. MacKay et al.[19] have also

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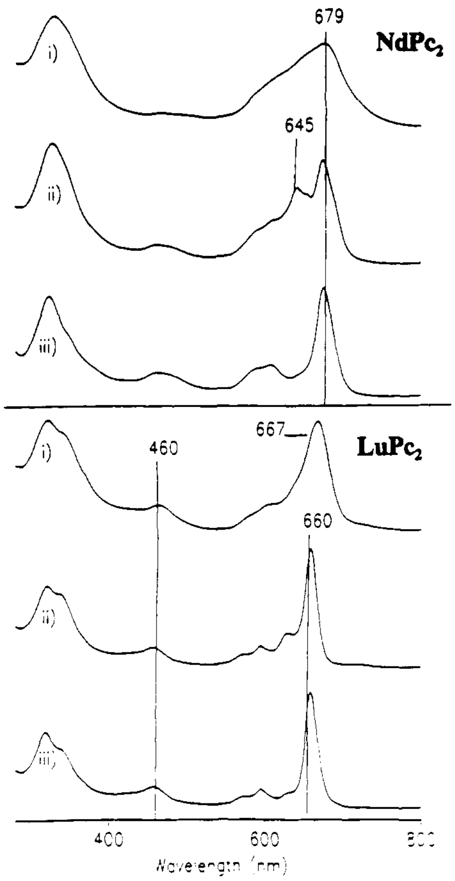

Figure 3. Visible spectra of an evaporated film of $NdPc_2$ (and $LuPc_2$): 200 nm thickness (i), solution of the film washed with benzene (ii), and of the starting material dissolved in benzene (iii).

isolated a green and blue bisphthalocyanine of gadolinium with the same spectral features as shown in Figures 1 and 2.

Thin Films of $LnPc_2$. One of the main objectives of our work is the preparation and characterization of submicron thin solid films of Pc materials. Using the green $LnPc_2$ compounds, thin solid films were fabricated by vacuum evaporation onto glass substrates. Green evaporated films were obtained from $LnPc_2$ (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) starting materials. The solid-state absorption spectra of the green films and the solution spectra of films dissolved in benzene were almost identical to the solution spectra of the starting material. The results are illustrated in Figure 3 for $LuPc_2$. Evaporation of $LnPc_2$ (Ln = Pr, Nd, Sm, and Eu), however, produced blue evaporated films. The absorption spectrum of a 200-nm thin film of $NdPc_2$ is shown in the top of Figure 3. The blue film was not completely soluble in benzene. A blue insoluble film remained on the glass slide which gave the unique electronic absorption spectrum of H_2Pc. The species that were soluble gave a blue-green solution with visible absorptions at 679 and 645 nm as shown in Figure 3. The latter absorptions were analogous to the Q-band spectral location in $NdPc^t_2$ and $NdHPc^t_2$ species, respectively. The N–H vibrational frequencies of H_2Pc were clearly observed in the infrared spectra of thin films of $LnPc_2$ (Ln = Pr, Nd, Sm, Eu) evaporated onto NaCl. The N–H fundamentals, however, were not seen in the IR spectrum of KBr pellets prepared with the starting $LnPc_2$ materials. The accumulated result in this section indicate that $LnPc_2$ with large ionic radius (i.e., Ln = Pr, Nd, Sm, Eu) form $LnPc_2$, $LnHPc_2$, and H_2Pc during evaporation.

Chemical Redox Effects on $LnPc^t_2$. The electrochemically reduced or "blue product" may be written as $[(Pc^t)^{2-}Ln^{3+}(Pc^t)^{2-}]^-$, and their spectral properties are dominated by the $(Pc^t)^{2-}$ anion which would make them spectrally similar to the mono-Pc complexes. Hafnium(IV), zirconium(IV), and uranium(IV) bisphthalocyanines contain two Pc^{2-} ligands. Their absorption spectra are similar to the blue $LnHPc^t_2$ materials. For example, the visible spectra of $HfPc_2$, $ZrPc_2$, and UPc_2 follow the pattern observed for the blue $LnHPc^t_2$, with a strong Q-band at 628 nm, a satellite band at 746 nm, and a clear window in the 500-nm region. Notably, complexes of Zr that contain a single Pc ligand (i.e., $ZrPcX_2$, X = anion) show a red-shifted Q band in comparison to $ZrPc_2$. The satellite band of $ZrPc_2$ at 746 nm was not observed in $ZrPcX_2$.

Chemical reduction of the green $LnPc^t_2$ material with hydrazine led to the reduced or "blue complex" of $LnPc^t_2$. The addition of an oxidative agent such as tetrachloro-1,2-benzoquinone regenerated the initial green material. Excess addition of oxidant to green $LnPc^t_2$ material produced the oxidized bisphthalocyanine or "red complex". The complete reversibility of the redox reaction was observed, and isobestic points in the visible spectrum were seen. The latter results are in agreement with chemical oxidation-reduction reported in $LuPc_2$.[18]

Vibrational Spectra. *Raman Spectra of Blue and Green Forms.* Langmuir–Blodgett monolayers of the green and blue materials were prepared and transferred to glass slides coated with 4 nm of gold or silver for surface-enhanced resonance Raman (SERRS) and surface-enhanced Raman (SERS) experiments. Resonant Raman scattering may be used to selectively probe the fundamental vibrations of the chromophore (macrocycle). To illustrate the characteristic pattern of relative intensities observed in the SERRS spectra of lanthanide series, the spectra of the green and blue materials of $HoPc^t_2$ are presented in Figure 4. The SERRS spectra of $HoPc^t_2$ have not been previously reported. It was found that SERRS for the $LnPc^t_2$ series was simply the enhanced RRS (resonant Raman scattering) without significant changes in relative intensities. The main difference between the SERRS (or RRS) spectra for the blue and the green materials is shown in the inset of Figure 4. The spectral differences observed with the 647.1-nm laser line (full resonance with the blue product) persisted in the SERRS spectra obtained with the 676.4-nm laser line (full resonance with the green) as shown in Figure 5. The strong band at 685 cm^{-1} has been assigned to the macrocycle breathing mode and is normally the most intense band in the SERRS (or RRS) of Pc molecules. Notably, in highly symmetric Pc molecules (i.e., those with D_{4h} point symmetry) the 685- and 747-cm^{-1} bands are seen (as in MgPc, CuPc, ZnPc). However, in the same spectral region of lower symmetry Pc complexes such as SnPc, VOPc, or (*tert*-butyl)$_4$VOPc which have C_{4x} point symmetry, three bands are observed: 685-cm^{-1} band (macrocycle breathing), and 723- and 747-cm^{-1} bands as noted in the blue $LnHPc^t_2$. The lower symmetry observed in the blue $LnHPc^t_2$ may result from two unequal Ln–Pc distances which could explain "the C_{4v} character" in the SERRS. The extra proton in the blue rare-earth bisphthalocyanine material could also account for the descent in symmetry. In a recent vibrational characterization of thin solid films of $DyPc_2$ and $HoPc_2$[20] it was found that the RRS of $DyPc_2$ presented the 677- and 740-cm^{-1} bands, while for the $HoPc_2$ vibrational frequencies were recorded

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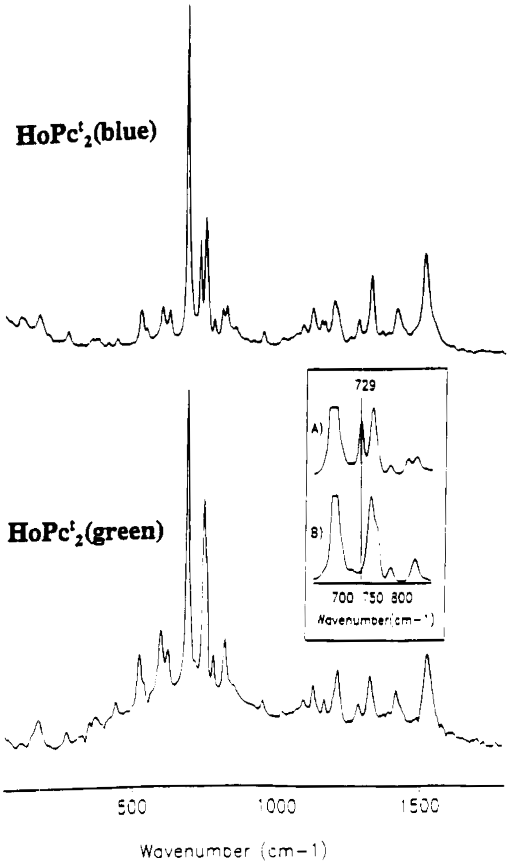

Figure 4. SERRS with the 647.1-nm laser line of one LB monolayer of HoPc$^t_2$ blue and one LB monolayer of HoPc$^t_2$ green on a Au island film. Spectral differences between the blue (A) and green (B) compounds are shown in the inset.

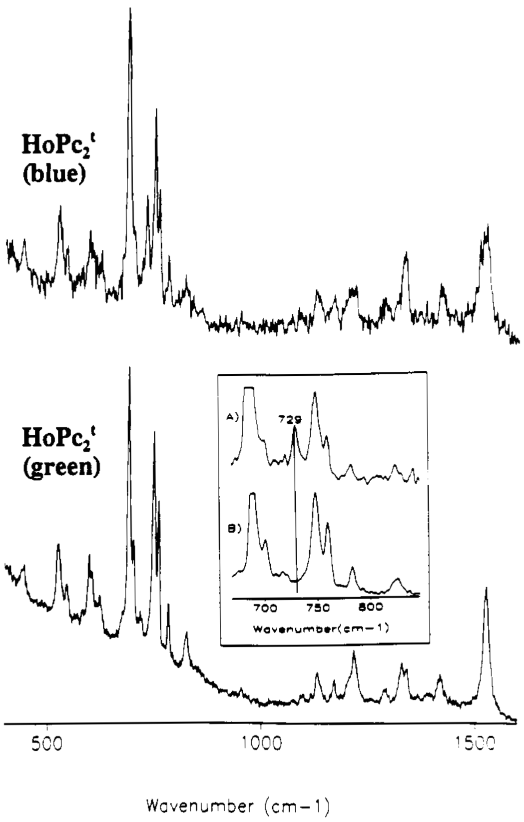

Figure 5. SERRS with the 676.4-nm laser line of one LB monolayer of HoHPc$^t_2$ blue and one LB monolayer of HoPc$^t_2$ green on a Au island film. The most significant spectral differences are expanded in the inset: (A) blue and (B) green.

at 679 and 743 cm^{-1}, with a weak band at 730 cm^{-1}. The results therefore suggested that the green starting material of HoPc$_2$ contained a small fraction of the blue compound. Similarly, in the resonant Raman spectra of LuPc$_2$ and YbPc$_2$,[21] bands at 679 and 740 cm^{-1} were found for YbPc$_2$, while LuPc$_2$ gave strong bands at 679 and 740 cm^{-1} with a very weak band at 731 cm^{-1}, that can be attributed to "blue contamination". The previous arguments are not conclusive; however, they represent the rationalization of a number of experimental findings that lead to symmetry differences between the green and blue complexes of octa-*tert*-butylbisphthalocyanines. For example, in the literature[22] the staggered configuration in bisphthalocyanines is not constant but extends from 37 to 45°. A D_{4d} structure can be envisioned in the totally symmetric case with perfect staggered configuration and equivalent Ln–Pc distances. Differences in the Ln–Pc distances would reduce the symmetry to C_{4v} or even lower, and the strong band at 730 cm^{-1} could derive its intensity from an allowed irreducible representation of a lower symmetry point group. The geometrical structure and symmetry of the green and blue products should nevertheless be considered an open question to be answered by further spectroscopic investigations. A comparative listing of fundamental vibrational frequencies observed for HoPc$^t_2$ green and blue is given in the Table II. The SERS of one LB monolayer of green and blue compounds on 4-nm Ag island films were recorded with the 514.5-nm laser line and the only difference was in the pattern of relative intensities. Fundamental vibrational frequencies were observed with the same frequency value in both blue and green compounds.

Infrared Spectra of Blue and Green Forms. The relative intensity pattern in the infrared spectra of the green LnPc$_2$ compounds has been shown to be very simple.[12,20,21] For instance, for LuPc$_2$ and YbPc$_2$ there were two very strong bands at 728 and 1322 cm^{-1} and one strong band at 1115 cm^{-1}. Similar bands were observed at 727, 1322, and 1114 cm^{-1} for DyPc$_2$ and HoPc$_2$. Clarisse and Riou[11] suggested that the 1322-cm^{-1} band would be the only characteristic band of the LnPc$_2$ complexes. In the MPc complexes the corresponding vibration is observed at 1330 cm^{-1}. The IR spectra of the green LnPc$^t_2$ and blue LnHPc$^t_2$ that we recorded showed differences in the pattern of relative intensities. For example, the IR spectrum of green LnPc$^t_2$ contained a strong band at 1318 cm^{-1} as illustrated in Figure 6A for HoPc$^t_2$. The relative intensity of this band decreased in the IR spectrum of the blue HoHPc$^t_2$ material as shown in Figure 6B. The other two frequencies of the LnPc$_2$ series (728 and 1115 cm^{-1}) which should have a large contribution from the C–H bending modes are no longer characteristic because of the partial C–H substitution by *tert*-butyl groups. Instead, a number of C–H bending vibrations of the alkyl moieties were observed. A strong band at ca. 1080 cm^{-1} was always observed in the IR spectra of the blue LnHPc$^t_2$ and LnHPc$_2$ materials. In fact the interconversion green → blue could be monitored by the intensity of the 1080-cm^{-1} band. A spectral analysis of MPc complexes indicated that this band may correspond to a characteristic frequency of the Pc^{2-} anion.[23,24] However, it should be pointed out that

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Table II. Observed Vibrational Frequencies of the Green and Blue Form of Holium Octa-*tert*-butylbisphthalocyanine[a]

green form		blue form		
IR	SERRS	IR	SERRS	assignment
	173 w		173 w	
	272 m		273 m	
	349 w		353 w	
	370 w		372 w	
	437 w		442 w	
	524 m		524 m	*t*-Bu def
	542 sh.		544 w	*t*-Bu def
	596 m		596 m	*t*-Bu def
	620 m		621 m	
674 w		674 w		
687 w	685 vs	689 w	683 vs	Pc breathing
700 w		697 w		
			728 s	
	747 s		750 s	Pc–ring
755 s	753 sh	755 vs		Pc–ring
782 w	781 m	782 w	780 m	Pc–ring
			809 m	
820 w	822 m		824 m	
833 m		830 s		*t*-Bu
855 w		855 w	855 w	
896 w		896 w		C–H bend (tb)
909 w		909 w		C–H bend (tb)
919 w		919 s	917 vw	C–H bend (tb)
953 w	951 w	953 w	951 m	benzene ring
1022 vw	1022 w	1022vw		C–C stretch (tb)
1047 w		1047 m		C–H bend (Pc)
1092 w	1095 w		1092 m	C–H bend (tb)
1100 w				
1128 vw	1127 m		1126	C–H bend (tb)
	1157 w		1158 w	
	1168 m		1169 w	
1201 w			1201 w	
1219 w	1214 m	1219 w		C–H bend (tb)
		1079 vs		Pc–ring
1256 m		1256 s		C–H bend (tb)
1282 m	1285 w	1282 m	1285 m	C–H bend (tb)
1318 vs		1322 s		C–H bend (Pc)
	1325 m		1328 m	pyrrole str
1363 m		1363 m	1367 w	C–H bend (tb)
1384 w				
1394 m			1394 m	
1412 m				
	1418 m		1420 m	isoindole stretch
1463 m		1463 w		
1482 w		1486 m		
1510 w				
			1517 m	pyrrole stretch
	1525 m			pyrrole stretch
1612 m		1612 m		benzene stretch
2863 w		2863 w		C–H stretch (tb)
2903 w		2902 w		C–H stretch (tb)
2957 m		2957 m		C–H stretch (tb)

[a] Infrared of a KBr pellet, and surface-enhanced Raman spectra observed with 647.1-nm excitation of one LB on Au.

the IR spectrum of the blue $LnHPc^t_2$ material than MPc complexes.

Thermal Interconversion of $LnPc^t$ Materials. Sublimation of the green material of $LnPc_2$ (Ln = Pr, Nd, Sm, Eu) produced films contaminated with the blue compound and H_2Pc. These products were identified by visible absorption and IR spectroscopy. The resonant Raman spectra of contaminated evaporated films of $LnPc_2$ (Ln = Pr, Nd, Sm, Eu) contained a band at 730 cm^{-1} which was observed only in the spectra of blue lanthanide bisphthalocyanine compounds. The 730-cm^{-1} band was, however, not present in the SERRS of one LB monolayer of the $LnPc_2$ (green material).

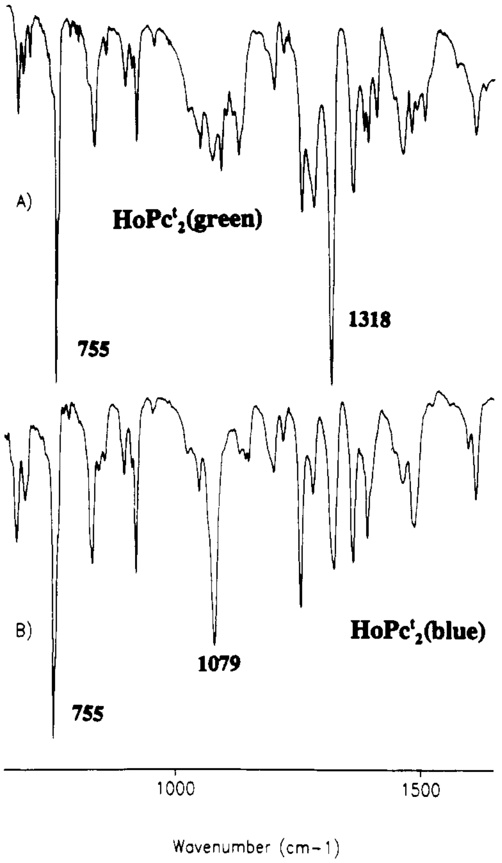

Figure 6. Transmission infrared spectra of $HoPc^t_2$ green (A) and $HoHPc^t_2$ blue (B) in a KBr pellet with instrument resolution of 1 cm^{-1}.

LB multilayer (4 LB on glass) films of the green $HoPc^t_2$ and blue $HoHPc^t_2$ were prepared for thermal studies. Heating the green LB film at 200 °C for 4 h in an oven produced an almost complete green → blue conversion. Similar results were obtained by heating a KBr pellet of the green form at 200 °C for 4 h. The infrared spectra of the KBr pellet of the green starting material was also used to monitor the green → blue conversion at different time intervals. A continuous increase of the relative intensity of the characteristic band of the blue material: 1079 cm^{-1} for $HoHPc^t_2$, and a decrease in the relative intensity of the 1318-cm^{-1} band was observed. In the latter case there was no spectroscopic evidence of H_2Pc^t formation.

Conclusions

The lanthanide series of bisphthalocyanine complexes of $LnPc^t_2$ (free-radical green material) and corresponding blue material ($LnHPc^t_2$) were characterized using Raman and surface-enhanced Raman scattering, infrared, and visible spectroscopy. EPR data for $HoPc^t_2$ and $TbPc^t_2$ confirmed the free-radical nature of the green $LnPc^t_2$ materials. The structure of the green $LnPc^t_2$ may have both Pc ligands symmetrically attached to the central metal atom. The presence of a proton in the blue compounds could account for lowering of symmetry as observed in the RRS (SERRS) spectra. The green compound of the early REE (Pr, Nd, Sm, Eu) are not stable during evaporation. Conversion of the green material to blue material was observed by heating LB assemblies and KBr pellets of the green material.

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