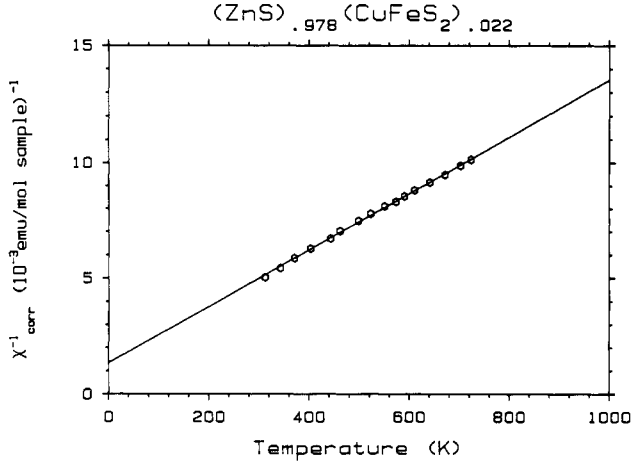

Figure 2. Variation of magnetic susceptibility with temperature for a single crystal of $(ZnS)_{0.978}(CuFeS_2)_{0.022}$.

magnetic measurements. The phase crystallized with the zincblende structure. Magnetic susceptibility measurements were made as functions of both field and temperature. Two separate crystals were measured and showed paramagnetic behavior without any field dependency at either room temperature or at liquid nitrogen temperature.

The reciprocal magnetic susceptibility of $(ZnS)_{0,978}(CuFeS_2)_{0,022}$ is plotted versus temperature in Figure 2 and approaches Curie–Weiss behavior with a Weiss constant of −110 K. The Curie constant obtained from the linear dependence of x^{-1} vs T shown in Figure 2 was standardized against a polycrystalline sample with 2.5 mol % $CuFeS_2$. Comparison with this standard gave a composition of 2.2 mol % $CuFeS_2$ for the single crystal. This composition is above the solubility limit of $CuFeS_2$ in ZnS single crystals reported by Moh.[3] This fact implies the presence of small clusters of an iron-rich phase, which would be consistent with the observed Weiss constant.

The properties of $(ZnS)_{0.978}(CuFeS_2)_{0.022}$ single crystals are summarized in Table II. They give the same IR transmission at the long-wavelength end, but there appears to be a cutoff at 5.0 μm. The microhardness and thermal stability data show that $CuFeS_2$ increases the hardness of pure ZnS and decreases the decomposition temperature.

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Registry No. $(ZnS)_{1-x}(CuAlS_2)_x$ (x = 0.027), 143120-96-1; $(ZnS)_{1-x}(CuAlS_2)_x$ (x = 0.069), 143120-97-2; $(ZnS)_{1-x}(CuInS_2)_x$ (x = 0.051), 143120-98-3; $(ZnS)_{1-x}(CuInS_2)_x$ (x = 0.105), 143120-99-4; $(ZnS)_{1-x}(CuFeS_2)_x$ (x = 0.022), 143121-00-0; ZnS, 1314-98-3.

Electrochromic Properties of Langmuir–Blodgett Films of Bisphthalocyanine Complexes of Rare Earth Elements

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The electrochromic behavior observed in the series of lanthanide bisphthalocyanine complexes with *tert*-butyl substituents $LnPc^t_2$ (Pc^t = R_4Pc, R = *tert*-butyl, Ln = Pr, Sm, Eu, Tb, Ho, Er, Tm, and Lu) is reported. The splitting of the first oxidation potential due to the proximity of the two phthalocyanine (Pc) rings was resolved in the voltammograms of Langmuir–Blodgett (LB) films. The LB films formed on ITO glass electrodes were more stable to repetitive cycling than cast films. Electrochromism was observed with LB and cast films electrodes in aqueous $KClO_4$ solution.

Introduction

The potential application of electrochromic materials, in multicolor electrochromic devices, has stimulated the investigation of the spectroelectrochemical properties of lanthanide (Ln) bisphthalocyanine derivatives.[1,2] Electrochromism of Langmuir–Blodgett (LB) films of unsubstituted bisphthalocyanine complexes of lanthanide elements ($LnPc_2$) has been studied for $LuPc_2$,[3] an octaalkoxymethyllutetium bisphthalocyanine,[4] and $YbPc_2$.[5] The electrochemical properties of the $LnPc_2$ complexes (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Er, Yb, Lu) in solution have also been reported.[6,7] The electrochromic properties of octa-*tert*-butylbisphthalocyanine complexes ($LnPc^t_2$, Ln = Er, Lu) deposited as LB films were recently documented by Liu et al.[1] The advantage of $LnPc^t_2$ materials over the unsubstituted $LnPc_2$ complexes is their enhanced solubility in organic solvents suitable for LB work. The synthesis of $LnPc^t_2$ or $LnPc_2$ can lead to a green

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free radical of general formula [$Pc^{2-}Ln^{3+}Pc^{-}$] and a blue product that may be assigned the general formula [$Pc^{2-}Ln^{3+}H^{+}Pc^{2-}$].[8,9] The spectroscopic characterization of the green and blue forms of octa-*tert*-butyl derivatives has been recently documented.[10] In the present work the electrochromic properties of LB films of the green and blue form of a series of octa-*tert*-butylbisphthalocyanines (Ln = Pr, Sm, Eu, Tb, Ho, Tm) are reported for the first time.

A Pc^{2-} ring may be reduced with up to four electrons which add to the $1e_g$ monoelectronic energy level.[11] The first and second oxidations result by sequential electron removal from the nondegenerate HOMO. The first oxidation potential determined by cyclic voltammetry or polarography has been tabulated for a number of metallophthalocyanines.[12] For instance, in ZnPc the first oxidation is known to occur at 700 mV (vs SCE) and at ca. 900 mV (vs SCE) for CuPc. In bisphthalocyanine complexes the $\pi-\pi$ orbital interactions between the two rings in the dimer may lead to a splitting of the first oxidation potential of the monophthalocyanine. Experimentally, two oxidation potentials of neutral $LnPc_2$ complexes in solution were reported by Konami et al.[6] They reported two waves occurring in the regions 100–300 and 550–700 mV with respect to a Ag/AgCl reference. The data published by Konami et al.[6] show that the splitting between the two oxidation potentials for a number of $LnPc_2$ complexes is relatively constant with a value of ca. 450 mV. Tomilova et al.[13] also have reported a splitting of about 450 mV between the first and second oxidations in a series of $LnPc^{t}_2$. The first oxidation corresponds to the blue → green color change and the second oxidation is the green → red color change. Similar separation between the two oxidation peaks (ca. 450 mV) was obtained for alkyl-substituted $LuPc_2$ complexes in dichloromethane.[14] For large aromatic systems, the chemical potential obtained in solution is assumed to be similar to those measured in thin solid films.[15] However, in the case of bisphthalocyanines the separation between the two oxidation peaks could be affected by the packing in the solid and the effect of the substituent on the Pc ring. Besbes et al.[4] reported a detailed electrochemical study of (octaalkoxymethylphthalocyaninato)$_2$Lu as thin solid films on a gold/alumina electrode with only one oxidation peak. It was found that the green → red step was characterized by well-shaped peaks in the voltammogram. However, the green → blue step was never well defined in thin solid films. Finally, in the solid state, CV of $LuPc_2$ LB layers on ITO electrode[3] and LB of $LnPc^{t}_2$ (Ln = Er, Lu)[1] showed that reversibility and electrochemical stability of the LB films was better than that of cast films.

Experimental Section

The synthesis of the green and blue forms of $LnPc^{t}_2$ and their separation have been previously reported.[9,10] The purified samples were kindly provided by Dr. L. Tomilova. Langmuir monolayers of neat $LnPc^{t}_2$ materials were spread from a toluene solution onto a subphase consisting of triply distilled water maintained at 15 °C by an external circulator. All LB work was conducted on a Lauda Langmuir film balance equipped with the electronically controlled Lauda FL-1 dipping device. ITO conducting glass was cleaned by washing with a mild detergent and thorough rinsing in distilled water. The glass was then dipped in acetone and dried with nitrogen gas. The Langmuir layer was compressed to 20 mN/m and transferred at a constant rate of 3 mm/min. A near-unity transfer ratio was always observed for the first LB layer. The second and subsequent monolayers were however transferred at 6 mm/min. The multilayer film ranged from 20 to 40 LB (LB = monolayer). Cast films were also prepared by covering the surface of an ITO electrode with a concentrated solution of $LnPc^{t}_2$ in toluene. The solvent evaporated within a few minutes to give a cast film.

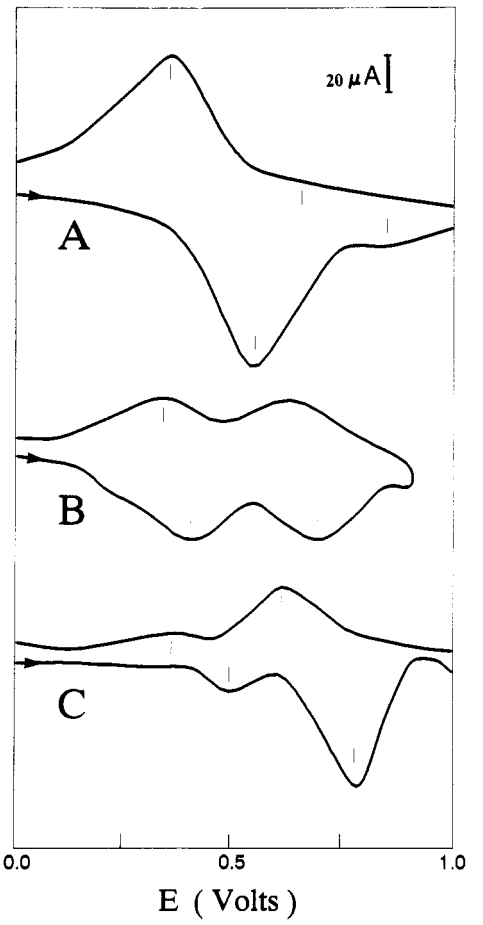

Figure 1. Cyclic voltammogram of an LB multilayer assembly of $HoPc^{t}_2$ on ITO glass. LB prepared with the green material (A), mixed of the two forms (B), and the blue material (C). Ag/AgCl reference and 100 mV/s scan rate.

Cyclic voltammetry (CV) was recorded in the conventional three-electrode cell and using an EG&G Princeton Applied Research Model 173 potentiostat galvanostat interfaced to an IBM-PC microcomputer. A platinum wire and Ag/AgCl electrode were used as the counter and reference electrodes. The electrolyte used in all the experiments was a 0.1 M solution of $KClO_4$. The electrolyte was degassed with high-purity argon prior to any electrochemical measurement.

A two-window cuvette was used to obtain the in situ electronic absorption spectra. Electronic absorption spectra were recorded on a Response UV–visible spectrophotometer interfaced to an IBM-PC computer. For data analysis, all files were imported to Spectra Calc software available from Galactic Ind. Corp.

Results and Discussion

Electrochemistry. Cyclic voltammetry (CV) and in situ UV–visible spectroscopy were used to study oxidation–reduction processes for $LnPc^{t}_2$ complexes in the form of LB films and cast films on an indium tin oxide (ITO)

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Table I. Oxidation Potentials ($E_{1/2}$ in mV) Observed for LB Films of Green and Blue Forms of $LnPc^t_2$ with a Ag/AgCl Reference Electrode (Scan Rate = 100 mV/s)

	LB of green form		LB of blue form	
material	E_1	E_2	E_1	E_2
$PrPc^t_2$	700			
$SmPc^t_2$	480	825	525	825
$EuPc^t_2$ (KCl)	700	950	690	1050
$TbPc^t_2$	510	775	450	750
$HoPc^t_2$	520	820	470	740
$ErPc^t_2$	600			
$TmPc^t_2$			460	750
$LuPc^t_2$	370	650	440	650

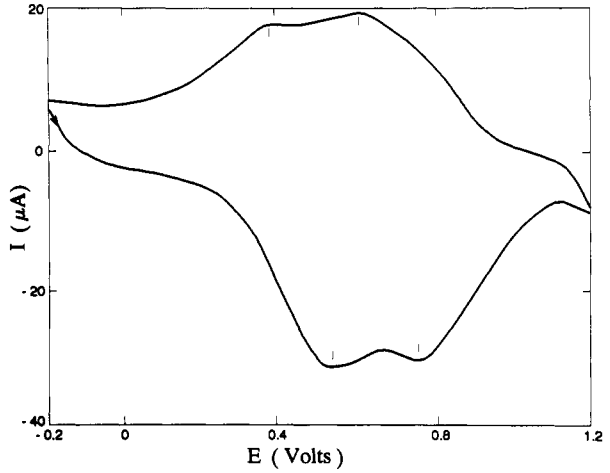

Figure 2. Cyclic voltammogram (100 mV/s) of an LB film of $LuPc^t_2$ fabricated with the blue material on ITO electrode.

electrode. In the present study, cyclic voltammograms were obtained for both the neutral blue $LnHPc^t_2$ and the neutral green $LnPc^t_2$ (Ln = Sm, Eu, Tb, Ho, Er, Tm, and Lu) fabricated as LB or cast films on ITO electrodes. The green free radical $[Pc^{t2-}Ln^{3+}Pc^{t-}]$ can be electrochemically reduced to the blue anion $[Pc^{t2-}Ln^{3+}Pc^{t2-}]^-$ or oxidized to form the red cation $[Pc^{t2-}Ln^{3+}Pc^{t-}]^+$. The two peaks in the cyclic voltammogram were resolved by decreasing the scan rate. The CV for an LB film fabricated with the green $HoPc^t_2$ material is shown in Figure 1A. The CV of an LB film of $HoPc^t_2$ made with a material containing a mixture of the green and blue forms is given in Figure 1B. It is important to notice that the neutral blue form obtained in the synthesis of $LnPc^t_2$, $[Pc^{t2-}Ln^{3+}H^+Pc^{t2-}]$, is different from the blue anion $[Pc^{t2-}Ln^{3+}Pc^{t2-}]^-$. Correspondingly, CV plots obtained for a blue $LnPc^t_2$ starting material were slightly different from the CV plots recorded for an LB fabricated with the green material as can be seen in Figure 1. The CV of an LB film fabricated with the blue $HoHPc^t_2$ is shown in Figure 1C. The collection of $E_{1/2}$ values for all compounds studied are given in Table I. For $PrPc^t_2$ the blue ↔ green interconversion readily occurs, and the value reported corresponds to one unresolved peak in the mixed material. The blue $SmHPc^t_2$ is stable. However, the green $SmPc^t_2$ seems to convert slowly into the blue and the films of green material contained a small amount of blue compound. A small separation (ca. 300 mV) between the two broad oxidation peaks was the trend observed in the voltammograms of the LB films. In solution the peaks were well resolved and separated by about 450 mV.[6,13] The separation of the two peaks in the cyclic voltammogram obtained for an LB film prepared with the blue $LuHPc^t_2$ is illustrated in Figure 2. In cast films, the observed peaks were even broader and a clear separation of the two oxidation waves was not possible. Furthermore, cyclic scanning of cast films was not reversible. The electrochemical

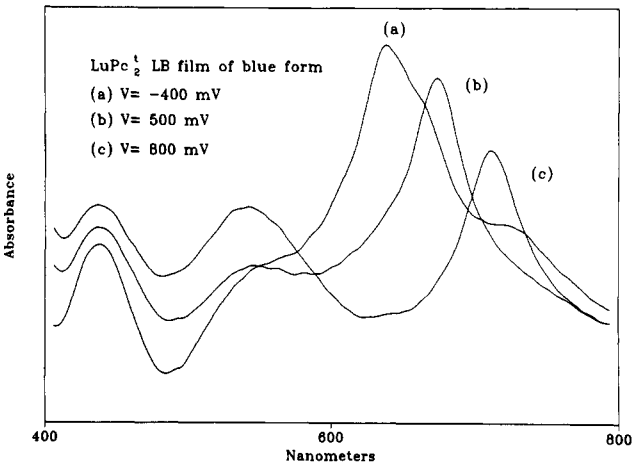

Figure 3. Electronic absorption spectra of $LuHPc^t_2$ LB assembly (blue material), recorded at three different electrode potential values.

stability of evaporated films of $LuPc_2$ has been reported by Collins and Schiffrin.[16] In the present work, repetitive cyclic scanning of LB films at 100 mV/s did not produce noticeable changes in the spectroelectrochemical properties of the LB film. For instance, voltammograms of LB films of $HoPc^t_2$ obtained after 750 cycles were identical to the initial CV. Positively, cycling between 0 and 1 V does not seem to alter the structure of LB films of $LnPc^t_2$. Similar results were obtained for voltammograms of LB films left in ambient for two weeks. For cast films, the first scan is usually different than the following scans, and the results were not reproducible. It was evident that LB films were more stable than cast films. The inhomogeneous structure of cast film inhibits the movement of solvent and ions through the film. In contrast, movement of solvent and ions seems to be much easier in the ordered environment of the LB film. Electron reduction peaks were not recorded for either LB or casted films. The in situ UV–visible spectroscopy was used to monitor the electron-transfer processes recorded in the CV.

Electrochromism. The electrochromic properties of $LnPc^t_2$ compounds allow the observations of at least three colored products: blue, green, and orange-red. Monophthalocyaninato (Pc) metal complexes are commonly blue with an absorption spectrum that contains a Soret band (ca. 300 nm) and a Q (600–700-nm region) absorption band. However, Pc complexes with transition metals show an additional absorption band ("charge-transfer transition") in the 500-nm region and appear green.[17] The strong absorption in the 500-nm region (green) has been associated with the presence of the Pc^- radical.[18] Notably, the Pc of rare-earth metals (LnPcX, X = anion) do not absorb in the 500-nm region. The absorption spectra of $LnPc^t_2$ complexes follow a characteristic pattern,[10] where the spectrum of the blue material has the typical Soret and Q absorption bands, while the spectrum of the green material contains an additional band (free radical band) in the 500-nm region. In situ UV–visible spectra of LB film on ITO transparent electrode were recorded at different potentials. The first reference spectrum of the LB film was taken in the absence of an external potential. After one cyclic scan, UV–visible spectra were taken at controlled

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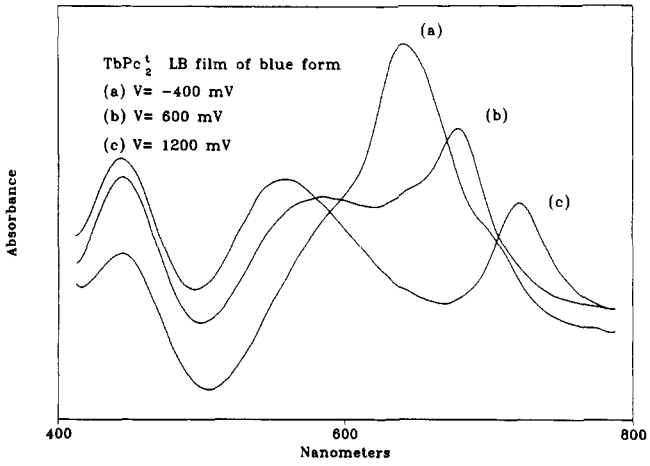

Figure 4. Changes in the visible spectrum of an LB assembly of $TbHPc^t_2$ (blue material) on ITO electrode with applied potentials.

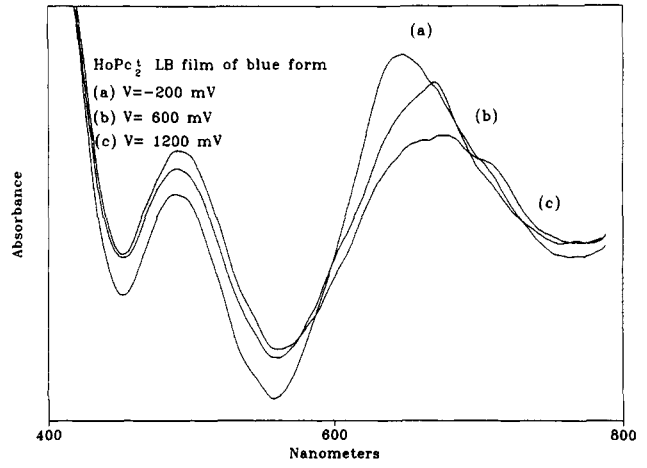

Figure 5. Visible spectra of an LB film of $HoHPc^t_2$ (blue material) on ITO electrode recorded at different applied potentials.

potential values. The electronic absorption spectra of an LB assembly (on ITO electrode) of the blue $LuHPc^t_2$ and $TbHPc^t_2$, measured in situ for a number of controlled electrode potentials, are shown in Figure 3 and 4. The multicolor electrochromism can also be observed visually. The $LuHPc^t_2$ blue (spectrum a in Figure 3) has a weak satellite of the Q band in the 700-nm region that has been observed for LB layers of Lu, Yb, Tm, Er.[10] However, the latter peak is not seen as a separate band in the spectrum of Tb (see Figure 4a), Dy, Ho, or lighter Ln complexes. The oxidized red form (c in Figures 3 and 4) is characterized by three well-defined absorptions at 450, 550, and 720 nm. The pattern seen in Figures 3 and 4 was not observed for all the complexes; instead two broad bands were recorded for an LB assembly of $HoPc^t_2$ as shown in Figure 5, and similar electrochromic effects were seen for $TmPc^t_2$ and $SmPc^t_2$ LB films.

The results of the electrochromic effect obtained for the LB films fabricated with the green $LnPc^t_2$ complexes

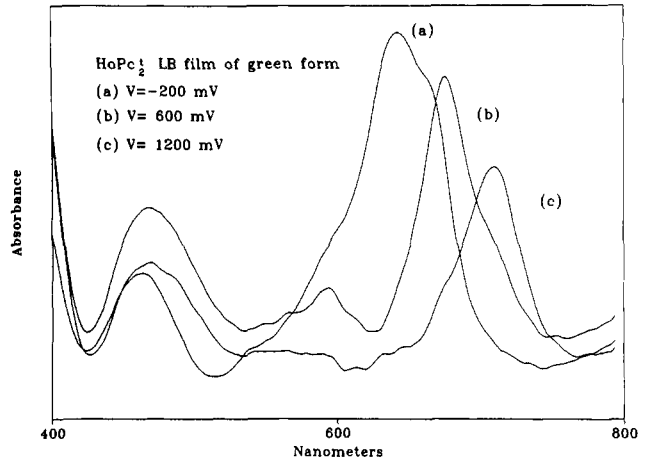

Figure 6. Electrochromic effect results for $HoPc^t_2$. LB assembly, prepared with the green material, on ITO electrode and 0.1 M $KClO_4$ solution.

presented a similar pattern. To illustrate the results, in Figure 6 the visible spectra of $HoPc^t_2$ green as a function of the applied potential are shown. In Figure 6, the spectrum 6a corresponds to the electrochemically produced blue (reduced form), 6b is the green, and 6c is the red. It should be pointed out that the blue → green interconversion readily occurs in the starting material of early Ln complexes, and LB assemblies fabricated with green materials contained a mixture of the two forms. Notably, the blue–green–red color change was also observed for cast films with unresolved oxidation peaks. Changes in the electronic spectra of cast films with the applied potential were similar to those presented in the figures.

Conclusions

Cyclic voltammograms of LB films of the green and blue forms of $LnPc^t_2$ complexes were obtained. The solid-state effect reduces the separation between the two oxidation peaks of bisphthalocyanine complexes. The electrochemical stability and reversibility of LB assemblies of $LnPc^t_2$ complexes in the region of oxidation processes was demonstrated. The electrochromic effect can be obtained with the green $LnPc^t_2$ material or with the blue $LnHPc^t_2$ material. The blue–green–red color changes may be observed in cast thin solid films even when the two oxidation processes may not be resolved in the voltammogram. The electron-transfer reactions modify the electronic distribution of the organic ring but the oxidation state of central metal atom is not affected. The results suggest that cast films would be less suitable for fabrication of stable electrochromic devices.

Acknowledgment. Financial assistance from NSERC of Canada is gratefully acknowledged. M.L.R. thanks the Ministry of Education and Science of Spain for a Research Fellowship.

Registry No. $PrPc^t_2$, 106856-36-4; $SmPc^t_2$, 112509-61-2; $EuPc^t_2$, 106856-34-2; $TbPc^t_2$, 106955-80-0; $HoPc^t_2$, 100842-61-3; $ErPc^t_2$, 84419-17-0; $TmPc^t_2$, 137597-38-7; $LuPc^t_2$, 84419-25-0.