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Synthesis, Characterization, Nonlinear Absorption and Electrochromic Properties of Double-Decker Octakis(mercaptopropylisobutyl-POSS)-phthalocyaninatolanthanide(III) Complexes

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In this study, the sandwich-like bis(phthalocyaninato)lanthanide(III) complexes MPc_2 (M = Lu, Gd) have been prepared. The reaction of 4,5-bis(mercaptopropylisobutyl-POSS)-phthalonitrile (**1**) [POSS: polyhedral oligomeric silsesquioxane] with lithium gave the dilithium octakis(mercaptopropylisobutyl-POSS)phthalocyaninate which was further reacted in situ with $Lu(OAc)_3{\cdot}3H_2O$ and $Gd(OAc)_3{\cdot}4H_2O$ in 1-pentanol to give compounds **2** and **3**, respectively. The structure of the target compounds was confirmed by elemental analysis, UV/Vis and IR spectroscopic as well as MALDI-TOF mass spectrometric techniques. The nonlinear absorption and optical limiting (OL) performance of **2** and **3** are investigated by means of the Z-scan technique. While **2** exhibits a good nonlinear absorption, **3** possesses a low nonlinear absorption. The ratio of the excited-state to ground-state absorption cross sections, κ, the effective nonlinear absorption coefficient, β_{eff}, and the energy density, F_{sat}, were determined for **2**. The results indicated that **2** possesses a good combination of optical limiting parameters.

Introduction

Polyhedral oligomeric silsesquioxanes (POSSs) are a class of condensed three-dimensional oligomeric organosiliceous compounds with cage frameworks having different degrees of symmetry. These molecular materials, in which each silicon atom is bound to one and a half oxygen atoms (sesqui-) and a hydrocarbon (-ane) leading to ($RSiO_{1.5}$) bond units, present the general formula $R_8Si_8O_{12}$.[1–3] In the field of nanostructural materials and composites, silsesquioxanes with close cages are currently studied both for the dispersion of these molecular materials in polymeric matrices and for the insertion of reactive organic functionalities suitable for chemical grafting reactions on siliceous supports.

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Sandwich-type compounds with tetravalent metal ions such as Sn^{4+}, Zr^{4+}, Th^{4+}, etc. are neutral double-decker complexes.[4,5] In contrast, lanthanide(III) metal ions and two tetrapyrrolic rings form a radical compound, in which one of the rings is a monoion and the other a dianion.[6,7] The paramagnetic nature of these radicals has been closely investigated with ESR spectroscopy, their semiconducting properties are an immediate consequence.[6,8] At the same time, these compounds display new infrared absorption bands, which have been related to the electronic interaction between the macrocycles. Accordingly, double-decker compounds, especially the lutetium derivatives, have generated a great deal of interest because of their potential applications as electrochromic materials,[9,10] their intrinsic conductivity[11–13] and optical nonlinearity,[14] and their potential use as gas sensors.[15–17] As the bulk characteristics of a molecular material are largely related to the properties of individual molecules, various modifications on these sandwich compounds have been made to improve their performance as advanced materials. Long alkyl side chains[18,19] and crown ether units[20] are two common functionalities added to the macrocycles to facilitate the formation of various mesophases and supramolecular structures.

Phthalocyanines (Pcs) have been shown to be one of the most promising optical limiting (OL) materials for nanosecond 532-nm laser pulses.[21–24] OL refers to a decrease in the optical transmittance of a material with increasing incident light intensity, which is considered a powerful means of protection for laser applications. Pcs have a relatively low

linear absorption and a high ratio of excited-state to ground-state absorption cross sections in the range 400–600 nm.[22] Pcs exhibit reverse saturable absorption (RSA),[25] which can limit the output energy of incident light effectively and they are used as optical limiters. The excellent properties of MPcs as candidates for OL applications originate not only from their extensive π-electron delocalization and their thermal and chemical stability, but also from their processability by either substituting the peripheral or the axial side groups or changing the central metal ion.[26] Very recently, we investigated nonlinear absorption of novel octakis(mercaptopropylisobutyl-POSS)-substituted MPcs (M = Co, Cu, and Zn).[27] Among them, CuPc has a very good nonlinear absorption and a very good combination of the OL parameters. It was found that heavy-metal atoms could facilitate intersystem crossing from the singlet state to the triplet state through spin–orbit coupling and thus reinforce the absorption of the triplet state with increased population.[22,28] In this paper, we studied nonlinear optical properties and optical limiting performance of octakis(mercaptopropylisobutyl-POSS)-substituted sandwich complexes of MPc_2 (M = Lu and Gd) to investigate the effect of heavy-metal atoms on the NLO properties.

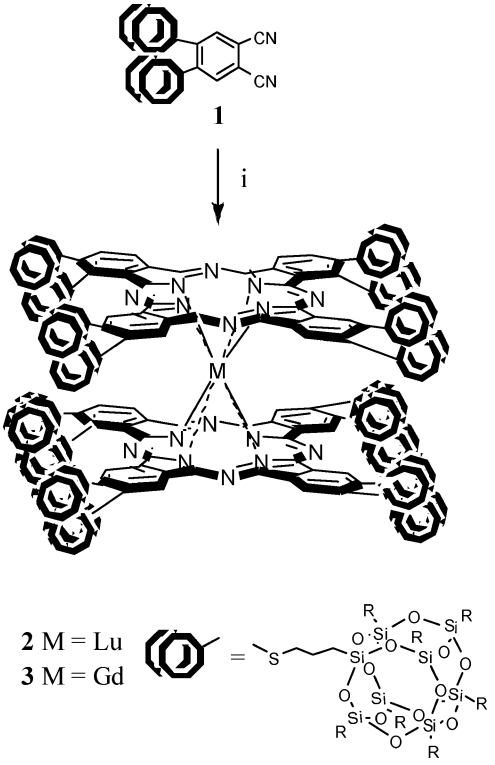
In our previous papers we have described oligonuclear and sandwich-type Pcs that carry various substituents.[29–33] These complexes show a wide range of interactions between the Pc rings, mainly depending on the metal center, bridging links, and the presence or absence of axial ligands. These species, having flexible bridging units, usually do not exhibit any measurable interaction, whereas rigid systems such as anthracene and naphthalene bridges exhibit strong interactions.

In this study, we describe novel sandwich-like bis(phthalocyaninato)lanthanide(III) complexes MPc_2 (M = Lu, Gd), which contain a mercaptopropylisobutyl-POSS functional group on each Pc moiety. The reaction of compound **1** with lithium gave the dilithium octakis(mercaptopropylisobutyl-POSS)phthalocyaninate, which was further reacted in situ with $Lu(OAc)_3·3H_2O$ and $Gd(OAc)_3·4H_2O$ in refluxing 1-pentanol to furnish compounds **2** and **3**, respectively. From the studies on the OL behavior of **2**, we found very good combinations of the OL parameters. Moreover, compound **2** displayed well-defined electrochromic behavior.

Results and Discussion

Synthesis and Characterization

The synthesis of our key starting material **1** was performed according to the literature method (Scheme 1).[27] The transformation of **1** into sandwich complexes **2** and **3** was carried out in a Schlenk system. Dilithiumphthalocyaninate generated by the reaction of **1** with lithium in refluxing 1-pentanol was reacted in situ with $Lu(OAc)_3·3H_2O$ and $Gd(OAc)_3·4H_2O$ to furnish sandwich complexes **2** and **3**, respectively, in moderate yields. Both compounds were obtained with sufficient purity and gave satisfactory analytical results.



Scheme 1. The synthetic pathway of MPc_2 (R = isobutyl; M = Lu for **2** and Gd for **3**). Reagents and conditions: (i) for compound **2**: lithium metal, $Lu(OAc)_3·3H_2O$, 1-pentanol, reflux; for compound **3**: lithium metal, $Gd(OAc)_3·4H_2O$, 1-pentanol, reflux.

Generally, Pc complexes are insoluble in most organic solvents. The solubility of the Pcs is affected by the central metal ions, and introduction of bulky groups such as POSS on the peripheral position of the Pc ring increases the solubility. Pc complexes **2** and **3** exhibit an excellent solubility in organic solvents such as chloroform and ethyl ether for **2** and pyridine, hot amyl alcohol, and ethyl ether for **3**.

The products were characterized by elemental analysis, IR and UV/Vis spectroscopy as well as MALDI-TOF mass spectrometry. IR spectroscopy has proved to be useful in characterizing the nature of the Pc ligand in tetrapyrrole sandwich complexes. The intense absorption at 1310–1320 cm^{-1} in neutral bis(phthalocyaninato) and mixed porphyrinatophyhalocyaninato rare earth(III) complexes containing one unpaired electron has been assigned to the $Pc^{–}$ IR marker band.[34] The typical IR marker band of the monoanion radical $Pc^{–}$ for **2** shows a strong band at 1320 cm^{-1} and is attributed to pyrrole C=C stretchings. The presence of the unpaired electron in **3** is also supported by the presence of a pyrrole stretching signal in the IR spectrum, which acts as the Pc monoanion radical marker band.[35] Along with the decrease in the ionic radii of the rare earth elements (REE), this band shifts to higher energy (1320 cm^{-1} for **2** and 1316 cm^{-1} for **3**).[36] In the IR spectrum of **2**, the disappearance of the strong C≡N stretching

vibration of precursor **1**[27] at 2215 cm^{-1} can be accepted as clear evidence for Pc formation. The IR spectra of **2** and **3** showed an Ar C=C peak at 1602 and 1595 cm^{-1}, respectively. IR spectroscopy can also be used to identify the substituents on the periphery of each Pc core; here the characteristic stretching vibrations attributable to –CH and CH_3 for **2** are observed at 2965–2960 cm^{-1} and for **3** at 2958–2932 cm^{-1}. They are in agreement with the structural information.

It is well documented that sandwich complexes MPc_2 can be formulated as $M^{3+}(Pc^{2-})(Pc^{-})$ or more precisely as $M^{3+}Pc_2^{3-}$, in which the unpaired electron is delocalized in both of the Pc rings.[37] NMR spectroscopy is a convenient and unambiguous method to elucidate the structures of the substituted diphthalocyanines. NMR spectroscopic data for these sandwich complexes are not abundant, probably because of their paramagnetism and also because of their poor solubility in common NMR solvents. Recently, L'Her and co-workers have shown that by adding hydrazine hydrate (1% v/v) to solutions of lutetium sandwich complexes in deuterated dimethylformamide or dimethylsulfoxide, satisfactory NMR spectroscopic data could be obtained. The neutral paramagnetic species were reduced to the corresponding anions, in which both of the macrocycles are diamagnetic dianions.[13] As compound **2** is sparingly soluble in $(CD_3)_2SO$, the spectrum was measured by using a similar strategy. The complex was dissolved in $CDCl_3$ and $(CD_3)_2SO$ (v/v 1:1) in the presence of ca 5% (v/v) hydrazine hydrate, but it was not possible to obtain satisfactory NMR spectroscopic results for **2**. This result may be due to the incomplete reduction of the neutral form of **2**, a fact which is consistent with the rather low value of its reduction potential.[38] Because of the strong paramagnetic nature of the metal center of gadolinium complex **3**, the ^1H NMR spectra of this complex could not be obtained.[39]

The matrix-assisted laser-desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of Lu complex **2** showed a prominent signal attributed to the molecular ion, but the molecular ion peak for Gd complex **3** could not be detected, which agrees with the relevant literature.[15] The MALDI-TOF mass spectrum of **2** is given in Figure 1, and the expanded protonated molecular ion peak region is given as inset in the MALDI-TOF mass spectrum. Although there are a high number of fragmentations, the protonated molecular ion peak intensity shows that **2** is sufficiently stable under laser firing and MALDI mass spectrometric conditions, and the quality of the spectrum was good enough to examine the protonated molecular ion peak. The MALDI-TOF mass spectrum of **2** could only be obtained with 1,8-dihydroxy-10*H*-anthracen-9-one (dithranol) but not with other MALDI matrices in the linear mode. Additionally, the matrix-to-analyte ratio was found to be very critical to obtain the protonated molecular ion peak in high intensity. The theoretical nominal mass of **2** was calculated and compared to the experimentally measured mass of the compound. It was found that the two masses exactly matched each other. This result shows that compound **2** is more stable under MALDI-MS conditions to analyze. No fragmentation was observed and also no impurity could be determined for **2**, because of the high stability and purity of this compound.

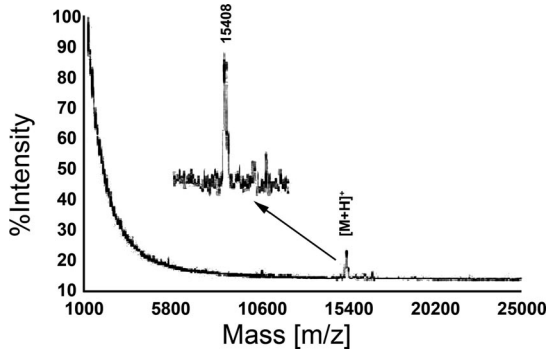


Figure 1. Positive ion mode MALDI-TOF mass spectrum of **2** in dithranol (1,8-dihydroxy-10*H*-anthracen-9-one) (20 mg/mL tetrahydrofuran) MALDI matrix by using a nitrogen laser and accumulating 100 laser shots. The inset spectrum shows the expanded molecular mass region of the complex.

The recording of electronic spectra is especially fruitful to establish the structure of **2** and **3** (Figure 2). When the electronic spectra of **2** were investigated, some peculiarities were observed. The electronic absorption spectrum of **2** was recorded in chloroform, and the data are given in the Experimental Section. The spectral features resembled those in our previous report,[33] except that all the absorption bands were significantly blueshifted, because of the different molecular symmetry. It can be seen from Figure 2 that compound **2** exhibits a split Soret band with two maxima at 307 and 350 nm,[33] which is analogous to those of the related counterparts $M(Pc)_2$. The Q band, which is attributed to the $\pi\rightarrow\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{2-} ring is split for **2**, giving an intense and blueshifted main band at 687 nm with comparable intensity and a redshifted satellite Q band (SQ) at 717 nm, and is additionally somewhat distorted leading to a third band of lower intensity at 659 nm in chloroform as shown in Figure 2. The splitting of the Q bands obviously reflects the extent of π–π interaction of the two Pc rings in compound **2**. This fully agrees with the result observed for the analogous Pc anions.[40] Compound **2** shows an additional band centered at 625 nm caused by aggregation of the Pc units through excitation coupling.[41] The characteristic absorption band for the radical Pc anion appears as a shoulder in the 400–500 nm region.[42] It is observed at 427 nm as a weak absorption band and is assigned to a transition of a full level to the singly occupied molecular orbital (SOMO).[43]

The electronic spectrum of gadolinium complex **3**, which was recorded in pyridine, shows a very broad Soret band at 352 nm. The characteristic Q band of **3** appears at 656 nm together with a satellite Q band at 703 nm (Figure 2). In addition, a rather broad band of lower intensity, which can be attributed to π-radical anion at 420 nm, is also observed.

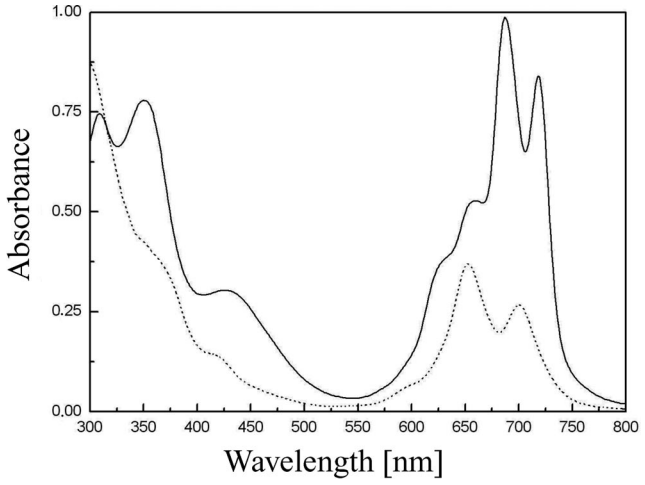


Figure 2. Absorption spectra for **2** in $CHCl_3$ (solid line) and for **3** in pyridine (dashed line).

Nonlinear Absorption and Optical Limiting Properties

The open-aperture Z-scan technique measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved along the optical axis of a convex lens.[44] The normalized transmission $T_{Norm}(z)$ as a function of the position along the z axis is given by:

$$T_{Norm}(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)}$$

where $q_0(z)$ is given by:

$$q_0(z) = \frac{\beta_{eff} I_0 L_{eff}}{1+(z/z_0)}$$

where z_0 is the diffraction length of the beam and $q_{00} \approx \beta_{eff} I_0 L_{eff}$, in which $L_{eff} \approx [1 - \exp(-\alpha_0 L)]/\alpha_0$, β_{eff} is the effective intensity-dependent nonlinear absorption coefficient and I_0 is the intensity of the light at focus. L_{eff} is known as the effective length of the sample and is defined in terms of the linear absorption coefficient, α_0, and the true optical path length through the sample, L. The open aperture spectra of **2** and **3** are given in Figure 3. The nonlinear absorption coefficients, β_{eff}, were calculated from the data by least-squares fitting of the equations above, and the waist radius of the beam was treated as a free parameter. Linear optical properties and optical limiting parameters of **2**, **3**, and fullerene are given in Table 1.

To fit the open aperture data and to obtain optical limiting parameters κ and F_{sat}, rate equations for a five-level system are solved; the nonlinear absorption coefficient is derived and put into the propagation formalism. Thereupon, normalized transmission as a function of fluency is obtained as follows:[45]

$$T(F,\kappa,F_{sat}) = \exp(-\alpha_0 L)\left(\frac{F_{sat} + \kappa T(F,\kappa,F_{sat})F}{F_{sat} + \kappa F}\right)^{1 - 1/\kappa}$$

The open aperture spectra are manipulated, and normalized transmissions (T_{Norm}) are plotted against energy density per pulse (F) for **2** (Figure 4).

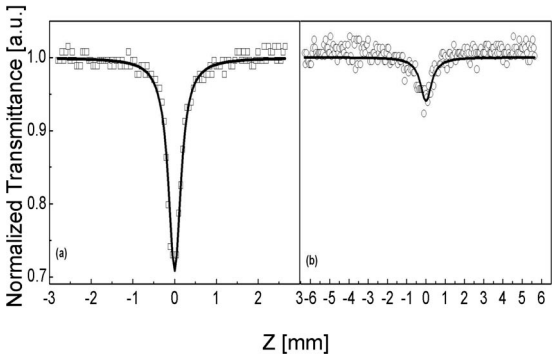


Figure 3. Normalized Z-scan experiment results for (a) $LuPc_2$ (**2**) and (b) $GdPc_2$ (**3**) under open aperture configuration at 0.11 mW input power. Solid lines represent theoretical fits.

Table 1. Linear optical properties and optical limiting parameters.

Compound	Solvent	α_0 [cm^{-1}]	I_0 [GW/cm^2]	β_{eff} [cm/W]	F_{sat} [J/cm^2]	κ [σ_{ex}/σ_0]	Ref.
C_{60}	toluene	2.81	0.5	6.6×10^{-8}	5.0	5.2	[47]
$LuPc_2$	chloroform	0.89	0.5	1.42×10^{-8}	6.3	15.3	this work
$GdPc_2$	pyridine	0.14	0.5	4.54×10^{-8}	–	–	this work

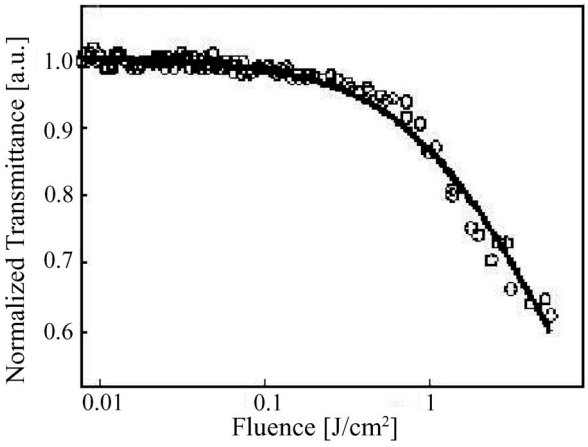


Figure 4. Plots of normalized transmission against incident pulse energy density for **2**. Solid lines represent theoretical fits.

Changing the central atom (metal) in a Pc can lead to a considerable variation of the relevant nonlinear optical properties and of the optical limiting performance.[25] Very recently, octakis(POSS)-substituted MPcs containing Co, Cu, and Zn were studied for OL. CuPc exhibited the largest nonlinear absorption of all investigated compounds while CoPc and ZnPc have a very low nonlinear absorption.[27] In this study, the effective nonlinear absorption coefficients of **2** and **3** are found to be 1.42×10^{-8} and 3.30×10^{-9} cm/W, respectively. Since compound **3** exhibited very low nonlinear absorption, we only studied the optical limiting performance of **2**. Wang et al. pointed out the importance of the atomic radius of rare earth elements in their optical limiting performance.[46] In that study, $Eu[Pc(OC_5H_{11})_8]_2$ ex-

hibited a better optical limiting performance, although Gd is a heavier atom than Eu. It was concluded that the bigger the ionic radius, the smaller the probability of π–π interaction, and therefore the longer the triplet state lifetime. However, Lu is a heavier rare earth element, and the optical limiting performance of compound **2** is better than that of compound **3**. On the other hand, heavy-metal atoms could facilitate intersystem crossing from singlet state to triplet state through spin–orbit coupling and thus reinforce the absorption of the triplet state by increased population.[22,28] The better optical limiting performance of compound **2** may be explained by spin–orbit coupling.

The OL efficiency of materials should be defined by a combination of some "yardsticks" such as the saturation energy density (F_{sat}), the ratio of the excited-state to ground-state absorption cross sections (κ), the effective nonlinear absorption coefficient (β_{eff}), and linear absorption coefficient (α_0). Note that a good optical limiter must have high κ, low F_{sat}, high β_{eff} and low α_0 values. To the best of our knowledge, since there is no study on the optical limiting performance of rare earth Pc complexes manipulated from open aperture Z-scan data, we can not compare the optical limiting performance of **2** with the literature. In a recent review, these values are taken into account for 40 materials.[47] It was found that β_{eff} ranges in the order of 10^{-10} to 10^{-8} cm/W, F_{sat} in the order of 1 to 170 J/cm^2 and κ in the order of 1 to 27. The investigated compound **2** has a very low linear absorption coefficient $\alpha_0 = 0.89$ cm^{-1}; it also exhibits a very high κ value of 15.3 (5.2[47] for fullerene), a β_{eff} value of 1.42×10^{-8} cm/W at 0.5 GW/cm^2 intensity (6.6×10^{-8} cm/W at 0.5 GW/cm^2[47] for fullerene) and a F_{sat} value of 6.3 J/cm^2 (5 J/cm^2[47] for fullerene). These results demonstrate that compound **2** exhibits good optical limiting behavior although CuPc, which has the same ligand as **2**, exhibits a better combination of OL parameters ($\alpha_0 = 0.89$ cm^{-1}, $\kappa = 12.5$, $\beta_{eff} = 7 \times 10^{-8}$ cm/W at 0.5 GW/cm^2 intensity and $F_{sat} = 0.85$ J/cm^2).[27]

Electrochemistry and Electrochromic Behavior

Cyclic voltammetry measurements for **2** were carried out on platinum in dichloromethane/tetrabutylammonium perchlorate (DCM/TBAP). The relevant data are given in Table 2. Compound **2** displays three reductions at $E_{1/2}$ = +0.21 V, $E_{1/2}$ = –0.56 V, and $E_{1/2}$ = –0.85 V, and a single oxidation at $E_{1/2}$ = +0.77 V vs. the saturated calomel electrode (SCE). Controlled-potential coulometry (CPC) studies showed that each redox process involves the transfer of one electron. A typical cyclic voltammogram for **2** at 0.050 V/s is shown in Figure 5 A. All redox couples of **2** are Pc-ring-based processes: only the cerium derivatives in the series of lanthanide double-deckers display a metal-centered redox process. However, the voltammetric behavior of **2** is considerably different from those of mono Pcs. At the positive potential side, the first redox process of mono Pcs (the first oxidation) involving the redox-inactive metal center usually occurs at potentials more positive than 0.7 V vs. SCE.[48] On the other hand, the first redox couple of **2** at the positive potential side occurs at a remarkably less positive potential, $E_{1/2}$ = +0.21 V vs. SCE, than those of mono Pcs. This process corresponds to the first reduction, since the HOMO is the SOMO and thus the first reduction is expected to occur at less negative potentials in sandwich-type complexes. Therefore, the other redox processes can be assigned accordingly as shown in Scheme 2. After the gain of one electron by the SOMO of a sandwich-type diphthalocyanine, a further electron is expected to be accepted by the LUMO. The separation between the first oxidation (couple IV) and the first reduction (couple I), $\Delta E_{1/2}$ in **2** is 0.56 V. $\Delta E_{1/2}$ values ranging from 1.36 to 1.70 V have been reported for monomeric Pc compounds,[48] which correspond to the gap between the HOMO and the LUMO. The low value for **2** is consistent with the values in literature.[49] It is due to the fact that the SOMO is responsible for both first reduction and first oxidation processes and reflects the ring–ring interactions in **2**. The voltammetric behavior of **2** implies that though it consists of free LuPc(–1)(Pc)(–2) radicals in the solid state, in solution at 0.00 V vs. the SCE, it is in the form Lu[Pc(–2)]$_2$ at the electrode/solution interphase, and one extra electron per molecule comes from the electrode set-up in the cell. On scanning towards positive potentials, firstly one-electron-reduced species are oxidized to their original state, LuPc(–1)Pc(–2), afterwards the first oxidation process of the original compound is monitored. we observed previously a similar type of behavior for a bis(double-decker) Pc compound.[50]

Table 2. Voltammetric data for **2**.

Solvent/condition	Redox couple	$E_{1/2}$[a] [V vs. SCE]	ΔE_p[b] [V]
DCM/TBAP	IV 1st oxidation	0.77	0.06
	I 1st reduction	0.21	0.12
	II 2nd reduction	–0.56	0.08
	III 3rd reduction	–0.85	0.10
DMSO/cast film/$KClO_4$	II	–1.07	0.14
	III	–1.48	0.16
DMSO/cast film/TBAP	II	–0.76[c]	–
	III	–0.89[c]	–

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.050 V/s. [b] $\Delta E_p = E_{pa} - E_{pc}$ at 0.050 V/s. [c] Cathodic peak potential for irreversible waves.

Cyclic voltammetry (CV) measurements were also carried out with an indium–tin oxide (ITO) electrode with a cast film of **2** (ca. 70 nm thickness) in dimethyl sulfoxide (DMSO)/$KClO_4$ and DMSO/TBAP (Table 2).

The voltammetric behavior of the film in DMSO/$KClO_4$ at the negative potential side is similar to that in DCM solution (Figure 5B). On scanning to negative potentials starting from 0.00 V, the green film of **2** displayed two reduction waves (IIc and IIIc), and the corresponding anodic waves were observed during the reverse scan. The green color of the film changed to blue when the potential scanned negatively, passing through couple II and it became dark blue to purple when the potential passed through couple III. The electrochromic response of the film was remarkably fast,

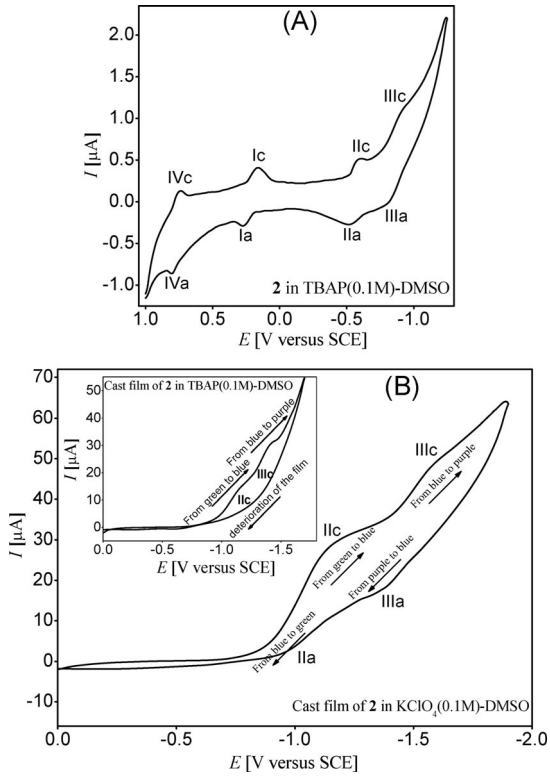


Figure 5. (A) Cyclic voltammogram of 1.00×10^{-4} M **2** at 0.050 V/s on Pt in DCM/TBAP; (B) cyclic voltammograms of cast films of **2** at 0.050 V/s on an ITO glass electrode in $KClO_4$(0.1 M)/DMSO (outset) and in TBAP(0.1 M)/DMSO (inset).

$$\{Lu[Pc(-1)]_2\}^+ \underset{(IV)}{\overset{e^-}{\rightleftarrows}} LuPc(-2)Pc(-1) \underset{(I)}{\overset{e^-}{\rightleftarrows}} \{Lu[Pc(-2)]_2\}^-$$

$$(II) \nwarrow\!\!\nearrow e^-$$

$$\{Lu[Pc(-3)]_2\}^{3-} \underset{(III)}{\overset{e^-}{\rightleftarrows}} [LuPc(-2)Pc(-3)]^{2-}$$

Scheme 2.

suggesting the presence of suitable ion channels through the cast film. It appears that small K^+ ions in solution can enter the film without a strong resistance to their movement. The voltammograms were generally stable for at least 50 cycles at the negative potential side after two or three initial "training" cycles. However, the cyclic voltammogram of the film of **2** collapsed at the positive side, and thus it was not possible to observe the color changes from green to orange or red.

When the CV curve was measured, altering the electrolyte from $KClO_4$ to TBAP in order to examine the influence of the electrolyte, electrochromic color changes were also observed, but only for the first scan. Moreover, the electrochromic response during the potential sweep towards more negative values was not reversible as judged by the absence of anodic waves on the reverse scan (inset in Figure 5B). Unfortunately, the cast film collapsed after several cycles. It appears that large tetrabutylammonium cations penetrating into the film during the cathodic sweep destroy the thin film while leaving it during the anodic sweep.

Some studies[51,52] on the film electrochemical properties of double-decker Lu^{III} Pcs reported that no reductions associated with the green-blue electrochromism were observed for $Lu[(C_nH_{2n+1}OCH_2)_8Pc]_2$ under the applied experimental conditions, although various types of films were utilized. But in the present study, the reversibility and electrochemical stability of the cast films of **2** in DMSO/$KClO_4$ were satisfactory demonstrated with the green-blue and blue-purple electrochromic transitions, although the preparation of homogeneous films on an electrode is difficult and a resulting inhomogeneous film may exhibit rather slow response of color change to the potential change and also easier separation from the electrode surface. The electrochromic response of **2** can be further enhanced by using other film preparation techniques such as spin coating, vapor deposition, and the Langmuir–Blodgett technique.

Conclusions

We have presented the synthesis, characterization, and nonlinear absorption of novel MPc_2s (M = Lu for **2** and Gd for **3**) by using compound **1** as a starting material, which was synthesized according to the literature method.[27] The new compounds were characterized by elemental analysis, IR and UV/Vis spectroscopy, and MALDI-TOF MS. Nonlinear optical experiments performed with the newly synthesized compounds suggest that both compounds show nonlinear absorption, and excellent combinations of the optical limiting parameters for **2** make it a very good candidate to act as an optical limiting material. The electrochemical measurements in the cast films suggest that compound **2** can be used as a component in electrochromic devices for the green-blue transition.

Experimental Section

General Remarks

All manipulations were carried out under an atmosphere of argon. Reagents and solvents, obtained from commercial suppliers, were of reagent-grade quality. The solvents were stored over molecular sieves (4 Å). 4,5-Bis(mercaptopropylisobutyl-POSS)phthalonitrile (**1**) was prepared by the literature method.[27] Column chromatography was used for the purification of compound **2**.

Routine IR spectra were recorded with a Shimadzu IR-470 Infrared spectrometer by using KBr pellets. Electronic spectra were aquired with a UNICAM UV 500 UV/Vis spectrometer. Elemental analysis was performed with LECO CHNS 932 in the Instrumental Analysis Laboratory of TÜBİTAK Ankara Research Center. Mass spectra were acquired with a Voyager-DE™ PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded in linear mode with an average of 100 shots. The MALDI matrix for **2** was prepared by dissolving dithranol (1,8-dihydroxy-10*H*-anthracen-9-one) (20 mg/mL) in tetrahydrofuran. The MALDI sample was prepared by mixing complex **2** (2 mg/mL in chloroform) with the matrix solution (1:10 v/v) in a 0.5-mL Eppendorf® microtube. Finally, 1 μL of this mixture was deposited on the sample plate, dried at room temperature, and then analyzed.

A Q-switched Nd:YAG laser (Quantel Brillant) was used as light source with a repetition rate of 10 Hz, a pulse width of 4 ns and a wavelength of 532 nm. The experimental technique used in the measurements was the Z-scan technique.[44] While the sample was moved through the focus, the transmitted open aperture signals were detected with a silicon detector. The Z-scan experiments were done with a 20 cm focal length lens. Complex **2** was dissolved in chloroform and complex **3** was dissolved in pyridine with a concentration of 1 g/L. All solutions were placed in a quartz cell with 1 mm optic path length. The linear absorption coefficients of **2** and **3** are 0.89 and 0.14 cm^{-1}, respectively.

Electrochemical measurements were carried out with a Princeton Applied Research Model VersoStat II potentiostat/galvanostat controlled by an external personal computer and by utilizing a three-electrode configuration at 25 °C. A platinum spiral wire was used as auxiliary electrode. The working electrode was made of platinum with an area of 0.12 cm^2 in the measurements in nonaqueous solution and an ITO conducting glass (12 ohm/cm^2) with an active area of 1.0 cm^2 in the measurements of cast film. The SCE was employed as reference electrode and separated from the bulk of the solution by a fritted glass bridge filled with a solvent/supporting electrolyte mixture. The ferrocene/ferrocenium couple (Fc/Fc^+) was additionally used as an internal standard, but the potentials were reported with respect to SCE. Solutions containing **2** were deoxygenated by a stream of high-purity nitrogen for at least 10 min before starting the experiment, and the solution was protected from air by a blanket of nitrogen during the experiment. The cast films were prepared on an ITO electrode directly by a hand-casting method. The cast film thickness was measured with a Horiba Jobin Yuan PZ 2000 ellipsometer. For the CPC studies, a platinum gauze working electrode, a platinum wire counter electrode separated with a bridge, a SCE as reference electrode, and a model 377/12 synchronous stirrer were used. Electrochemical grade TBAP and $KClO_4$ (Merck, extra pure) were used as supporting electrolytes. Extra pure DCM was used as solvent in the electrochemical measurements.

Bis[octakis(mercaptopropylisobutyl-POSS)phthalocyaninato]lutetium(III) (2): Clean lithium metal (0.014 g, 2 mmol) was placed in a sealed glass tube with 1-pentanol (2 mL), and the mixture was stirred at 90 °C until the complete dissolution of lithium. Compound **1** (0.275 g, 0.145 mmol) was then added to the reaction mixture, which initially turned yellow, then rapidly green-blue. Afterwards, the mixture was heated at reflux for 1 h, and to this mixture was added $Lu(OAc)_3{\cdot}3H_2O$ (0.050 g, 0.142 mmol). The final mixture was heated at reflux for an additional 20 h. After the reaction mixture had been cooled to room temperature, it was added to a mixture of water/ethanol (2:5, v/v, 14 mL) in order to precipitate the product. The precipitate was filtered off and washed several times with water, ethanol, acetonitrile, and acetic acid. Then, the crude product was dissolved in chloroform (25 mL) and it was filtered. After the filtrate had been concentrated to dryness, the residue was washed with ethanol and acetone and it was dried in vacuo (90 °C). The crude product was purified by using chromatography with silica gel and eluted with chloroform. The resulting compound was soluble in chloroform and diethyl ether, sparingly soluble in DMSO, but insoluble in ethanol, acetonitrile, acetic acid, and acetone. Yield: 5.3 mg (2%). M.p. > 300 °C. UV/Vis (chloroform, 0.5 μM): λ_{max} ($\log\varepsilon$) = 307 (4.171), 350 (4.193), 427 (3.783), 625 (3.859), 659 (4.022), 687 (4.295), 717 (4.221) nm. IR (KBr): $\tilde{\nu}$ = 2965–2960 (aliph. –CH and CH_3), 2860, 1602 (Ar C=C), 1550, 1462, 1400, 1332, 1320, 1229, 1115, 840, 738, 486 cm^{-1}. MS (MALDI-TOF): m/z = 15408 $[M + H]^+$. $C_{560}H_{1120}LuN_{16}O_{192}S_{16}Si_{128}$ (15407): calcd. C 43.61, H 7.26, N 1.45, S 3.32; found C 43.52, H 7.14, N 1.34, S 3.38.

Bis[octakis(mercaptopropylisobutyl-POSS)phthalocyaninato]gadolinium(III) (3): Clean lithium metal (0.0057 g, 0.813 mmol) was placed in a sealed glass tube with 1-pentanol (2 mL), and the mixture was stirred at 90 °C until the complete dissolution of lithium. Compound **1** (0.525 g, 0.275 mmol) was then added to the reaction mixture, which initially turned yellow, then rapidly green-blue. Afterwards, the mixture was heated at reflux for 4 h, and to this mixture was added $Gd(OAc)_3{\cdot}4H_2O$ (0.075 g, 0.224 mmol). The final mixture was heated at reflux for an additional 30 h. After the reaction mixture had been cooled to room temperature, it was added to a mixture of water/ethanol (1:2, v/v, 21 mL) in order to precipitate the product. The precipitate was filtered off, washed several times with water, ethanol, chloroform, ethyl acetate, and acetone, and it was dried in vacuo (90 °C). This compound is moderately soluble in hot pyridine, hot amyl alcohol, and ethyl ether. Yield: 91 mg (17%). M.p. > 300 °C. UV/Vis (pyridine, 0.65 μM): λ_{max} ($\log\varepsilon$) = 352 (3.809), 420 (3.330), 656 (3.744), 703 (3.607) nm. IR (KBr): $\tilde{\nu}$ = 2958–2932 (aliph. –CH and CH_3), 2870, 1595 (Ar C=C), 1552, 1462, 1400, 1330, 1316, 1227, 1114, 839, 739, 484 cm^{-1}. $C_{560}H_{1120}GdN_{16}O_{192}S_{16}Si_{128}$ (15389): calcd. C 43.66, H 7.27, N 1.45, S 3.32; found C 43.57, H 7.22, N 1.37, S 3.25.

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