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# Synthesis, Characterization, Electrochemical, and Optic Limiting Properties of Novel Co$^{II}$, Cu$^{II}$, and Double-Decker Lu$^{III}$ Phthalocyanines

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The synthesis, spectroscopic, electrochemical, and optical properties of tetrasubstituted Co$^{II}$, Cu$^{II}$, and double-decker Lu$^{III}$ phthalocyanines are reported. The new compounds were characterized by elemental analysis, IR and UV/Vis spectroscopy, and MALDI TOF mass spectrometry. Their electrochemistry was studied by cyclic voltammetry and Osteryoung square-wave voltammetry in nonaqueous medium. Nonlinear absorption and optical limiting performance of peripheral-substituted $(C_{30}H_{28}N_30)_4Co$ (**5**), $(C_{30}H_{28}N_30)_4Cu$ (**6**), and $[(C_{30}H_{28}N_30)_4]_2Lu$ (**7**) were investigated by the Z-scan technique. Whereas **6** and **7** showed good nonlinear absorption, **5** did not. Optical limiting parameters of the ratio of the excited state to the ground state absorption cross sections $\kappa$, the effective nonlinear absorption coefficient $\beta_{eff}$, the linear absorption coefficient $\alpha_0$, limiting threshold $F_{th}$, and the saturation density or energy density $F_{sat}$ values were determined for **6** and **7**. The results indicated that both compounds exhibited good optical limiting performances.

## Introduction

Rare-earth diphthalocyanines, especially the lutetium derivative, have become objects of intense investigation.[1–4] Owing to the characteristic overlapping of the ligand π orbitals of rare-earth diphthalocyanine compounds, these compounds possess a wide range of unique properties, which makes them suitable for a variety of applications.[5,6] Many of these applications depend on the nature of the metal ion incorporated at the center of the phthalocyaninato ring as well as the substituents on the macrocycle. The characteristics of sandwich complexes are largely related to the properties of the individual molecules. Various modifications have been made on these compounds with the goal of improving their properties as advanced materials. Long alkyl side chains[7–9] and crown ether[10,11] units are two common functionalities added to the macrocycles to facilitate the formation of various mesophase supramolecular structures.

As a result of the intermolecular interaction between the macrocycles, peripherally unsubstituted metal phthalocyanines are practically insoluble in common organic solvents, which therefore minimizes their applications. The solubility of phthalocyanines can be improved by introduction of substituents on the peripheral and nonperipheral sites of the phthalocyanine ring.

Although there are several ways to synthesize bis(phthalocyaninato)lanthanide complexes, common features include the relatively high temperatures and long reaction times required in comparison to monomeric phthalocyanines.[4] Recently, Pushkarev and co-workers[2] suggested a new synthesis method for the preparation of heteroleptic bis- and tris(phthalocyanine) compounds in high yields. These complexes display unique physical, spectroscopic, and electrochemical properties. Among these, bis(phthalocyaninato)lutetium complexes have especially generated a great deal of interest due to their potential use as electrochromic materials[12–14] and due to their intrinsic conductivity[15] and optical nonlinearity;[16–19] these materials may also be used as gas sensors[20,21] and field-effect transistors (FETs), and in display technologies.[22,23]

Among the nonlinear optical applications of phthalocyanines, their optical limiting (OL) performance is the most promising.[24,25] The phenomenon of optical limiting is based on attenuating the light beam when it exceeds a threshold value and transmitting the ambient light with low absorption. Optically sensitive elements, especially the human eye, are hence protected. Optical limiting based on re-

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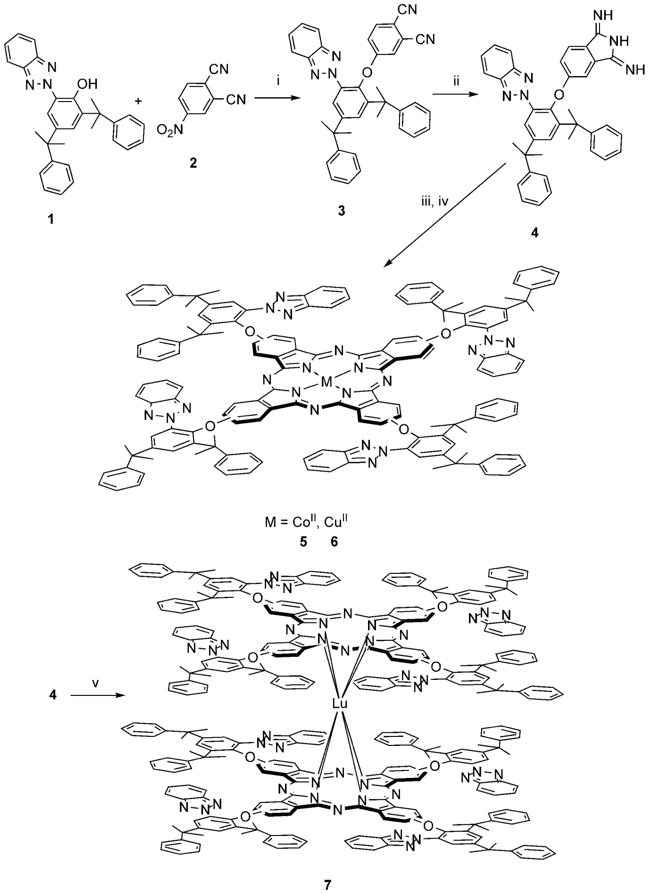
verse saturable absorption in phthalocyanines has been largely reported in the literature both on the nanosecond and picosecond time scales at a wavelength of 532 nm.[26–29] The excellent properties of metal phthalocyanines (MPcs) as candidates for optical limiting applications originated not only from their extensive π-electron delocalization and their thermal and chemical stability, but also from their processability either by substituting the peripheral or axial side groups or by changing the central metal ion. A change in the central metal atom in a Pc can lead to considerable variation in the relevant nonlinear optical properties (NLO) and OL properties.[24]

In this study, the synthesis, characterization, and optic limiting properties of novel Co$^{II}$ (**5**), Cu$^{II}$ (**6**), and double-decker Lu$^{III}$ phthalocyanine (**7**) are reported. Whereas lutetium and copper phthalocyanine complexes exhibit the largest nonlinear absorption, the cobalt phthalocyanine compound showed very low nonlinear absorption.

## Results and Discussion

### Synthesis and Characterization

Starting from **1** and **2**, compound **3** was obtained in 65% yield by a base-catalyzed nucleophilic nitro group displacement reaction. The reaction was carried out in a single step by using $K_2CO_3$ as the nitro displacing base at 70–90 °C in dry DMF under an argon atmosphere. The reaction of **3** with ammonia in methanol by the catalysis of sodium methoxide at reflux temperature gave compound **4** in 90% yield. Phthalocyanine complexes of **5** and **6** were prepared by the general synthetic route given in Scheme 1. Bis(phthalocyaninato)lutetium(III) complex was prepared by the reaction of **4** and lutetium(III)acetate monohydrate in octanol, catalyzed by DBU at elevated temperatures under an argon atmosphere for 12 h. The mixture was then precipitated in water (250 mL). Product **7** was obtained and isolated by column chromatography on silica gel (THF/methanol, 10:1) in 25% yield. Compounds **5**, **6**, and **7** are soluble in acetone, chloroform, DCM, THF, DMF, and DMSO.



Scheme 1. (i) $K_2CO_3$, DMF, Ar; (ii) $NH_3$, $CH_3ONa$; (iii) $Co(CH_3COO)_2{\cdot}4H_2O$, DMF, Ar; (iv) $Cu(CH_3COO)_2{\cdot}2H_2O$, DMF, Ar; (v) $Lu(CH_3COO)_3{\cdot}H_2O$, DBU, octanol, Ar.

The spectroscopic characterization of newly synthesized compounds performed by $^1$H NMR, IR, and UV/Vis spectroscopy and mass spectrometry are in accordance with the proposed structures. The IR spectrum of **3** exhibits characteristic frequencies at 3110–3008 (Ar-H), 2900–2840 ($CH_3$), 2226 (C≡N), 1594–1486 (C=C), 1250–1278 (Ar-O-C), and 1495 and 1457 cm$^{-1}$ (Ar-H). The absence of a nitrile peak at 2226 cm$^{-1}$ in **3** and the emergence of new peaks at 3500–3200 (N-H) and 1650 cm$^{-1}$ (=NH) are a good indication of the formation of **4**. The IR spectrum of **5** exhibit two bands at 3083 and 3053 cm$^{-1}$ and are assigned to the symmetric and asymmetric stretching vibration of –CH in the aromatic ring, and those at 2965, 2927 and 2852, 2874 cm$^{-1}$ are assigned to the symmetric and asymmetric stretching vibration of alkyl –CH groups. The band appearing at 1601 cm$^{-1}$ was assigned to the aromatic C=C stretching vibration and those at 1494 cm$^{-1}$ to the stretching vibration of C=N.[30] A peak for the substituted benzene ring appeared at 747 cm$^{-1}$. The aromatic C-H bending vibrations appeared at 1400 and 1273 cm$^{-1}$. The band at 700 cm$^{-1}$ was assigned to the C–C macrocycle ring deformation.[31] The $^1$H NMR spectra were also in good agreement with the synthesized compounds. The $^1$H NMR spectrum of compound **3** has two singlet at 1.72 and 1.86 ppm, corresponding to two methyl groups each. The aromatic protons appeared between 6.76 and 7.84 ppm corresponding to 18 protons. Compound **4** has a similar $^1$H NMR spectrum to that of **3** except for the =NH protons, which appeared at 8.5 ppm as a broad peak to confirm the presence of the =NH group.

The UV/Vis spectra of **5** and **6** in THF displayed characteristic absorption bands around 615 and 680 nm in the Q-band region (Figure 1). The Q-band was attributed to a π→π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. The other band (B band) in the UV region at 335 nm is due to the transition from the deeper π levels to the LUMO.

Double-decker complexes are regarded as single-hole complexes in which an unpaired electron is present in one of the macrocyclic ligands.[32,33] The UV/Vis spectra of **7** taken in THF, showed the characteristic double-decker phthalocyanine lutetium complex with the Q-band at 684 nm and weak vibronic band at 615 nm that is responsi-

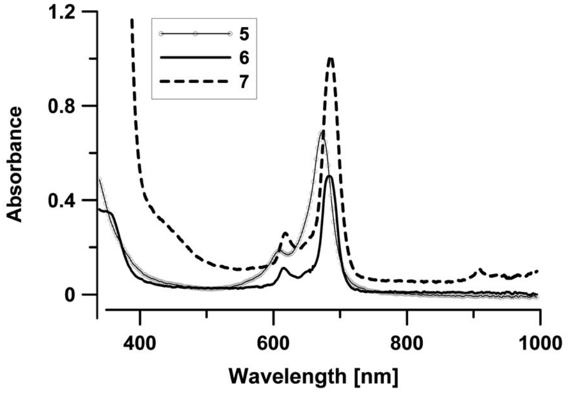


Figure 1. UV/Vis spectra of **5**, **6**, and **7** in THF.

ble for the color of the compound (Figure 1). For the homoleptic bis(phthalocyaninato)lutetium(III) complexes, two weak π–radical–anion bands near 450 (shoulder) and 910 nm are also seen. This is the characteristic absorption band for double-decker (phthalocyaninato)rare-earth(III) complexes, which arises due to the transition from the forth-occupied HOMO to the SOMO and from the SOMO to the LUMO, respectively.[33–35] The other band in the UV region of the spectrum at 370 nm (B band) arises from the transition of the deeper π level to the LUMO of conjugated 18π electron systems.[3]

High-resolution MALDI mass spectra of all complexes were obtained by using the positive ion and reflectron mode in various novel MALDI matrices, and one of them is given in Figure 2 for **7** as an example. The high-resolution MALDI mass spectra of the complexes were obtained in IAA, DNB, and dithranol matrices for **5**, **6**, and **7**, respectively. Isotopic molecular ion peak distributions of the complexes were calculated and compared to the theoretical distributions of the complexes. It was found that all theoretical isotopic distributions of the complexes were matched exactly with the experimental results. These experimental isotopic peak distributions of the protonated molecular ions is given as the inset spectrum in Figure 2.

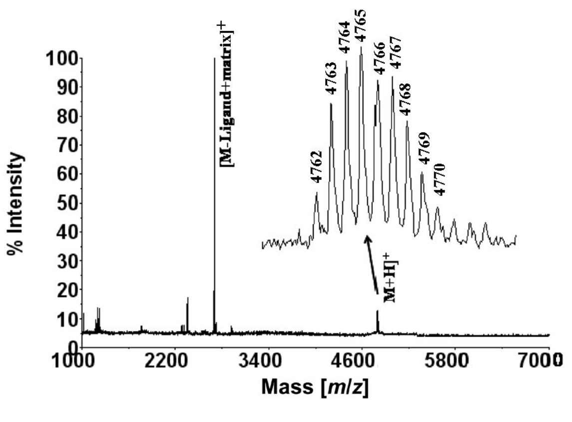


Figure 2. The positive-ion and reflectron mode MALDI-MS spectrum of **7** (lutetium) was obtained in dithranol (1,8-dihydroxy-10*H*-anthracen-9-one) (20 mg mL$^{-1}$ tetrahydrofuran) MALDI matrix by using nitrogen laser accumulating 50 laser shots. Inset spectrum shows expanded molecular mass region of the complex.

Besides the protonated molecular ion peak of the complexes, only very few peaks at low intensities were observed as fragmented ions. However, the clean spectra showed the high stability of these complexes under the laser shots and mass spectrometric conditions and also the high purity of the synthesized complexes.

## Electrochemical Measurements

The voltammetric measurements of **5**, **6**, and **7** were carried out on a glassy carbon (GC) electrode in DCM or DMF, tetrabutylammonium tetrafluoroborate (TBATFB) as supporting electrolyte by cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (SWV). The relevant data are given in Table 1. All lanthanide bis(phthalocyanine) complexes can undergo multiple reductions of the conjugated macrocycle. The electrochemical behavior of **5** was investigated in DCM by CV and SWV. Compound **5** showed both oxidation and reductions waves labeled $O_1$ and $O_2$ and $R_1$, $R_2$, and $R_3$ within the electrochemical window of DCM containing 0.1 M TBATFB. All These processes can be attributed to the successive addition and removal of one electron to ligand-based orbitals of the bis(phthalocyaninato) complex.[36–38] The measured half-wave redox potentials for **5** in DCM solution containing TBATFB as the supporting electrolyte are listed in Table 1, which also includes selected data from the literature for the related compounds. Osteryoung SWV of **5** in the same medium displayed oxidation and reduction potentials more clearly. Three reductions waves labeled $R_1$, $R_2$, and $R_3$, $E_{1/2}$ = –0.10, –1.30, and –1.70, with two oxidation waves labeled $O_1$ and $O_2$, $E_{1/2}$ = 0.32 and 0.64 V vs. Fc/Fc$^+$ have been observed, respectively. The separation between the reduction and oxidation peak potentials and the variation in the peak potentials with the scan rate for all the processes lies between 60 and 90 mV, showing their reversible or quasireversible nature.

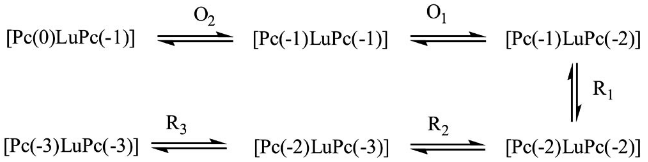
The HOMO level of bis(phthalocyaninato) complexes results from a splitting of the $4a_u$ π-HOMO of the monophthalocyanine due to interactions between both rings and leads to a complex whose HOMO is occupied by only one electron, giving a radical character to the compound. These types of compounds should be reducible by a total of five electrons.[34] The bis(phthalocyaninato)rare-earth(III) complexes are known to be radicals, and the HOMO is semi-occupied (SOMO). The absorption band at 920 nm in the electronic spectrum is attributed to the electronic transition from the SOMO to the degenerate LUMO.[37] Because the HOMO is the semi-occupied molecular orbital (SOMO) in sandwich-type phthalocyanine complexes, the first reduction of **5** occurs at much lower reduction potentials than those of monophthalocyanines. The first ring reduction of monomeric phthalocyanine occurs usually at potentials more negative than –0.60 V vs. SCE.[5] In contrast, compound **5** is reduced at a potential that is considerably more

Table 1. Redox potentials of Lu[($C_{30}H_{28}N_3O$)$_4$]$_2$ and selected double-decker (phthalocyaninato)lutetium(III) complexes.

| Compounds | Solvent/Supporting electrolyte | RE[a] | $O_2$ | $O_1$ | $R_1$ | $R_2$ | $R_3$ | $\Delta E_1$ | Ref.[b] |
|---|---|---|---|---|---|---|---|---|---|
| Lu[($C_{30}H_{28}N_3O$)$_4$]$_2$ | DCM/TBATFB | Fc/Fc$^+$ | 0.64 | 0.32 | –0.10 | –1.30 | –1.70 | 0.42 | tw |
| Lu$_2$[(Pc)(–2)(Pc)(–1)]$_2$ | THF/TBAP | Fc/Fc$^+$ | | 0.34 | –0.06 | –0.84 | –1.14 | 0.40 | [12] |
| MPc$_2$ | DCM/TBAP | SCE | | 0.40 | –0.02 | –1.10 | –1.33 | 0.42 | [37] |
| Lu(Pc)$_2$ | PhCN/TBAPF$_6$ | Fc/Fc$^+$ | | –0.05 | –0.46 | –1.54 | –1.92 | 0.41 | [38] |
| Lu$_2$Pc$_4$ | DCM/TBAP | Fc/Fc$^+$ | | 0.06 | –0.32 | –1.09 | –1.31 | 0.40 | [44] |
| CoPc | DMF/TBATFB | Fc/Fc$^+$ | 0.44 | 0.01 | –0.88 | –2.03 | –2.43 | 0.89 | tw |
| CuPc | DMF/TBATFB | Fc/Fc$^+$ | 0.15 | –0.10 | –1.42 | –1.94 | | 1.32 | tw |

[a] RE: Reference electrode, $\Delta E_1 = O_1 - R_1$, at 0.100 V s$^{-1}$ scan rate. [b] tw: this work.

positive with respect to that of monophthalocyanines. The electrochemical properties of **5** are similar to those of previously reported double-decker lutetium phthalocyanine compounds. This can be revealed by the similar potential difference between the first oxidation and the first reduction potentials, $\Delta E°_{1/2}$ and between the first of the first reduction and the second reduction processes $\Delta E°_{1/2} = 0.42$ V, which also have good agreement with the previously reported results of the bis(phthalocyaninato)lutetium compounds recorded in DCM.[39–41] The electrode reactions of **5** are schematically shown in Scheme 2.



Scheme 2. The one-electron redox processes of Lu[($C_{30}H_{28}N_3O$)$_4$]$_2$.

The difference in the redox potentials of $O_1$ and $R_1$ ($\Delta E_1$) represents the energy for putting a second electron in the SOMO of the neutral double-decker radical [M(Pc)$_2$] or to remove one of the two electrons from the HOMO of the reduced species [M(Pc)$_2$]$^-$.[37] As the first oxidation step and first reduction step involve the HOMO and the LUMO of the molecule, the energy difference between these two redox processes corresponds to its electrochemical molecular bandgap. The peak separations and the variation of the peak potentials with the scan rate for these redox processes were usually within the range of quasireversible behavior, which indicates that the complex has potential to be a molecular semiconductor.[42,43] Solubility in common organic solvents, thermal stability up to 300 °C, and the small electron-pairing energy necessary for the bis(phthalocyaninato)lutetium(III) complex makes it a good candidate to find application in electronics.

In contrast to the HOMO level of double-decker or bis(phthalocyanine)s, the LUMO of monometallophthalocyanines has doubly degenerate $e_g$ symmetry and can therefore accept up to four electrons.[39] The redox properties of **6** and **7** were studied by using CV and SWV in DMF, and typical voltammograms of **6** and **7** are shown in Figures 3 and 4. The potential values and assignments are summarized in Table 1. Complex **6** showed good voltammetric behavior, with five redox processes ($E_{1/2}$ vs. Fc/Fc$^+$) labeled $O_2$ = 0.440 V, $O_1$ = 0.01 V, $R_1$ = –0.88 V, $R_2$ = –2.030 V, and $R_3$ = –2.425 V. The first reduction and first oxidation processes are metal based in polar coordinating solvents, which is a well-known electrochemical behavior of CoPc complexes in coordinating solvents such as DMF and DMSO.[45] Therefore, the first reduction and the first oxidation of **6** could be assigned to Co$^{III}$(Pc–2)/Co$^{II}$(Pc–2) ($O_1$) and Co$^{II}$(Pc–2)/Co$^{I}$(Pc–2) ($R_1$) redox couples and the second and the third reductions and the second oxidation processes are Pc-ring-based and assigned to Co$^{I}$(Pc–2)/Co$^{I}$-(Pc–3) ($R_2$), Co$^{I}$(Pc–3)/Co$^{I}$(Pc–4) ($R_3$), and Co$^{III}$(Pc–1)/Co$^{III}$(Pc–2) ($O_2$), respectively. The separation between the metal center reduction and oxidation processes ($O_1$–$R_1$ = 0.89 V), which reflects the HOMO–LUMO gap of the complex, is comparable to the reported CoPc complexes.[42] The number of electrons transferred for each redox process is determined by the chronocoulometric studies and it showed that each redox process is approximately equal to unity. Therefore, the electrochemical reactions corresponding to all waves in the voltammogram are stepwise one-electron processes. The ratios of the anodic to cathodic peak currents ($i_a$ to $i_c$) for couples for all the waves are close to unity, suggesting a reversible/quasireversible redox processes.

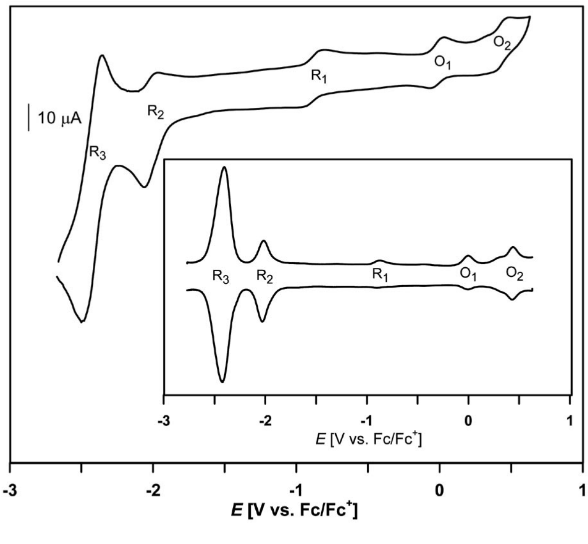


Figure 3. Cyclic and square-wave (inset) voltammograms of **6** in DMF containing 0.1 M TBAFB, scan rate: 100 mV s$^{-1}$.

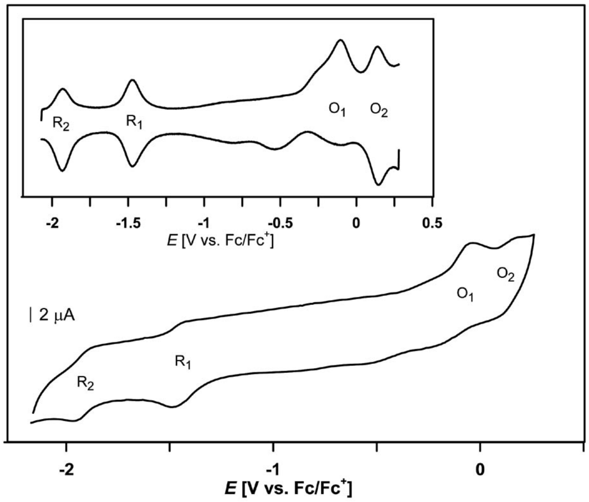


Figure 4. Cyclic and square-wave (inset) voltammograms of **7** in DMF containing 0.1 M TBAFB, scan rate: 100 mV s$^{-1}$.

Figure 4 represents the CV and SW voltammogram of **7** and they display four redox processes assigned to the phthalocyanine ring oxidation and reduction, labeled $O_2$, $O_1$, $R_1$, and $R_2$. The first and second reduction waves were observed at –1.42 and –1.94 V and the oxidation waves appeared at –0.10 and 0.15 V, respectively, at a scan rate of 0.100 V s$^{-1}$. Osteryoung SW voltammogram of **7** suggests that all four redox processes have quasireversible character (Figure 4). The separation of the firs reduction and the first oxidation processes (–1.32 V) reflects the HOMO–LUMO gap of the CuPc complexes. Although $R_1$, $R_2$, and $O_2$ seem to be reversible processes, $O_1$ of **7** is quasireversible, which is illustrated by the SW voltammogram of the complex comparing the anodic to cathodic peak current.

The good optical limiting properties of phthalocyanines arise from their extensive π-electron delocalization, good chemical and thermal stabilities, and also from their great opportunity to be tailored by either substituting a metal atom to the core and/or by substituting different peripheral and axial ligands. Especially, changing the metal atom has tremendous effect on optical limiting performance of the Pc compound.[24] In this study, this strategy has been followed by changing the metal atom with Lu, Cu, and Co while keeping the substitution groups the same. Among these compounds, **6** and **7** exhibited good optical limiting performance, but **5** did not show any optical limiting behavior. Blau and co-workers presented the values of optical limiting parameters of structurally different phthalocyanine derivatives containing Zn$^{II}$, Co$^{II}$, Ni$^{II}$, Pd$^{II}$, Ga$^{II}$, and In$^{III}$ metal atoms manipulated by the Z-scan technique.[27] In this study, CoPc or NiPc monomers are found out to be the weakest nonlinear absorbers among the 39 different kinds of investigated Pc compounds.

From open aperture Z-scan experimental data, nonlinear absorption coefficients of **6** and **7** were calculated at various focal intensities by using the theory previously reported.[46] The normalized transmission as a function of position $z$, $T_{Norm}(z)$, is given by:

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

where $q_0(z)$ is given by:

$$q_0(z) = \frac{\beta_{eff} I_0 L_{eff}}{1 + (z/z_0)^2}$$

where $z_0$ is the Rayleigh range of the beam and $l_{eff}$ is the effective sample length containing linear absorption coefficient, $\alpha_0$ and true optical path through the sample, L inside.

The open-aperture spectra of **6** and **7** are given in Figure 5. The effective nonlinear absorption coefficients are depicted as a function of the focal intensity. The decrease in $\beta_I$ with an increase in focal intensity can be attributed to the fact that higher odd order nonlinear absorptions take part. In order to compare with the literature, $\beta_I$ values at $I_0$ = 0.5 GW cm$^{-2}$ were found from the $\beta_I$–$I_0$ graphs.[26]

To fit the open-aperture data and obtain optical limiting parameters $\kappa$ and $F_{Sat}$, rate equations for a five-level system were solved; nonlinear absorption coefficients were derived and inserted into a propagation formalism. Then normalized transmission as a function of fluence is obtained as follows:[47]

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

The open-aperture spectra were manipulated and normalized transmissions ($T_{Norm}$) were plotted against energy density per pulse ($F$) for **6** and **7** by using the above equation (Figure 6).

It is not reasonable to characterize the optical limiting performance by only one parameter, such as $\beta_I$. Preferably, the optical limiting efficiency of materials should be defined with 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 ($\kappa$), besides the effective nonlinear absorption coefficient ($\beta_I$). Note that a good optical limiter must have high $\kappa$, low $F_{sat}$, and high $\beta_{eff}$ values. In comparison to the literature, it is not easy to estimate which Pcs will be the better optical limiters, as most of the materials do not satisfy all the conditions for good optical limiting behavior.

Rare-earth-substituted phthalocyanines are sandwich-type compounds where the metal resides between two Pc rings. To the best of our knowledge, there are no studies on the optical limiting performance of rare-earth-substituted phthalocyanines manipulated from open-aperture Z-scan data to obtain $\kappa$, $F_{sat}$, and $\beta_{eff}$ values. Therefore, we can only compare the nonlinear absorption coefficient $\beta_I$ with the literature. The wavelength dependence of the nonlinear absorption coefficient of a bis(phthalocyanine) NdPc$_2$ was studied.[48] Compound **7** has almost the same nonlinear absorption coefficient as that of NdPc$_2$ measured at 532 nm.

In a recent review,[26] optical limiting parameters ($\beta_{eff}$, $\alpha_0$, $F_{Sat}$, and $\kappa$) are taken into account for 39 materials. In this review, it was found that $\beta_{eff}$ ranges in the order of $10^{-10}$ to $10^{-8}$ cm W$^{-1}$, $F_{Sat}$ in the order of 1 to 170 J cm$^{-2}$, and $\kappa$ in

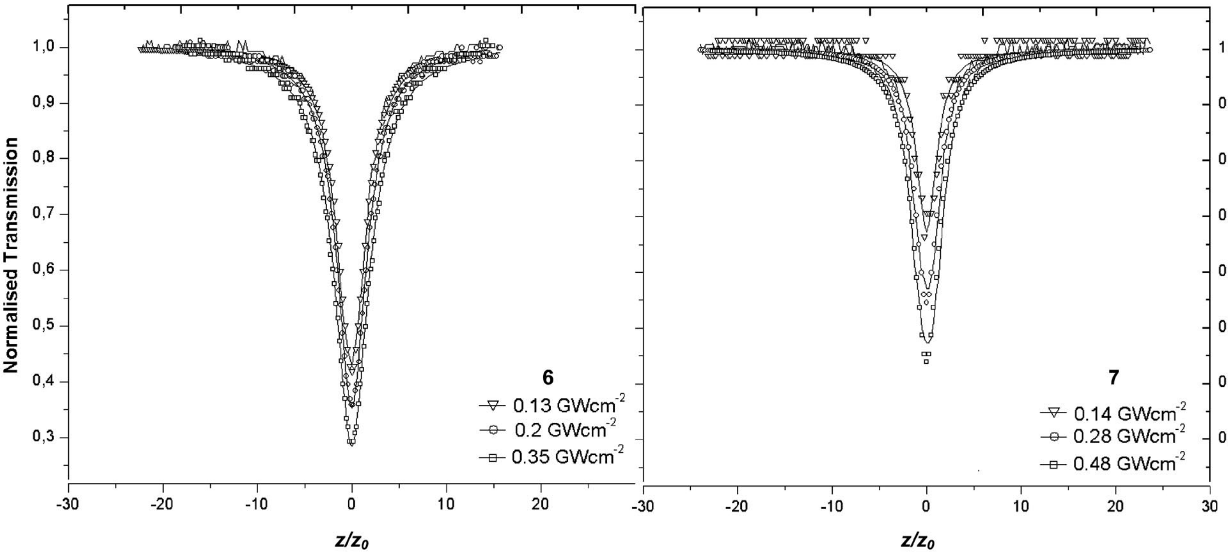


Figure 5. Normalized Z-scan experiment results for **6** and **7** under open-aperture configuration. Solid lines represent theoretical fits.

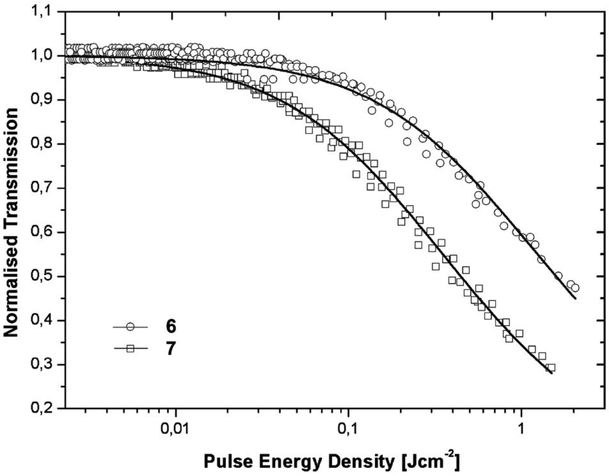


Figure 6. Plots of normalized transmission against incident pulse energy density for **6** and **7**. Solid lines represent theoretical fits.

the order of 1 to 27. Investigated compound **7** has a high $\beta_I$ value ($7.76 \times 10^{-8}$ cm W$^{-1}$), a very high $\kappa$ value (15.3), and a low $F_{Sat}$ value (2.98 J cm$^{-2}$). Wang et al. pointed out the importance of the atomic radii of rare-earth elements on the optical limiting performance.[49] In this study, although Gd was a heavier atom than Eu, Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$ exhibited better optical limiting performance. It was concluded that the bigger the ion radius, the smaller the probability of π–π interactions and, therefore, the longer the triplet-state lifetime. Despite the fact that Lu is a light rare-earth element, compound **7** exhibits good optical limiting performance.

As the linear absorption coefficient of compound **6** is close to that of (Ciso$_5$H$_{11}$)$_8$Cu with isopentyl substitution groups,[26] one can compare the OL performances of these compounds. Compound **6** exhibits a high $\kappa$ value of 13.6 [$\kappa$ value for (Ciso$_5$H$_{11}$)$_8$Cu is 8.8], low $F_{sat}$ value of 0.98 J cm$^{-2}$ [$F_{sat}$ value for (Ciso$_5$H$_{11}$)$_8$Cu is 4.6 J cm$^{-2}$], and high $\beta_{eff}$ value of $1.9 \times 10^{-7}$ cm W$^{-1}$ at 0.5 GW cm$^{-2}$ intensity [$\beta_{eff}$ value for (Ciso$_5$H$_{11}$)$_8$Cu is $6.4 \times 10^{-8}$ cm W$^{-1}$ at 0.5 GW cm$^{-2}$ intensity].

OL is a nonlinear effect consisting of a decrease in the transmittance of a sample under high intensity or fluence illumination. Ideally, the transmitted intensity should remain constant (or even decrease to a small value) above a certain limiting threshold. The nonlinear response should possess a low limiting threshold. Therefore, the limiting threshold ($F_{th}$) is also taken into account as an optical limiting parameter. In the literature, the $F_{th}$ value is usually greater than 1 J cm$^{-2}$.[24,26,50] Compound **6** exhibits very low $F_{th}$ value of 0.5 J cm$^{-2}$. The $F_{th}$ value for the investigated LuPc$_2$ compound was found to be 1.8 J cm$^{-2}$, and this value is comparable with that of EuPc$_2$.[50]

## Conclusions

In conclusion, both compounds have a good combination of optical limiting parameters between a relatively high absorption cross section $\kappa$, a very low energy dependent saturation $F_{sat}$, a relatively high effective nonlinear absorption coefficient $\beta_{eff}$, and a low limiting threshold $F_{th}$. The OL performances of both compounds may be attributed to the effectiveness of peripheral side groups as a result of the improved electron mobility.

In this work, the synthesis, characterization, and optical limiting properties of new bis(phthalocyaninato)cobalt(II), -copper(II), and sandwich -lutetium(III) complexes were accomplished. Electrochemical studies of **5** showed that the complex undergoes five redox couples with a HOMO–LUMO gap of $\Delta E_{1/2}$ = 0.42 V. Solubility in common organic solvents, thermal stability up to 300 °C, and the small electron-pairing energy necessary for **5**, make it a good candidate for electronic applications. Complex **6** showed good voltammetric behavior, with five redox processes; the first reduction and first oxidation processes are metal based. Complex **7** displayed four redox processes, all assigned to the phthalocyanine ring oxidation and reduction.

It was found that, although both bis(phthalocyaninato) copper(II) and -lutetium(III) complexes have good optical limiting properties, (phthalocyaninato)cobalt(II) in contrast did not.

## Experimental Section

**General Remarks:** All chemicals used were reagent grade. The solvents were purified according to standard procedures[51] and stored over molecular sieves. Electrochemical grade tetrabutylammonium tetrafluoroborate (TBAFB) (Fluka) was used as the supporting electrolyte in voltammetric measurements in nonaqueous solvents. Compound **1** was obtained from Aldrich. Compounds **2**, **3**,and **4** were prepared according to literature procedures.[52] Melting points were determined with a Electrothermal Digital melting point apparatus (Model IA9100). FTIR spectra were recorded with a Mattson 1000 FTIR spectrometer in the range 400–4000 $cm^{-1}$ as KBr disks. $^1H$ NMR spectra were determined with a Gemini Varian 200 MHz NMR spectrometer. Electronic absorption spectra were measured in THF with an Ocean Optics HR2000 CG UV-NIR diode array UV/Vis spectrometer in the range 200–1100 nm. Cyclic and square-wave voltammograms were carried out by using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA. A three-electrode system was used for CV and SWV measurements in dichloromethane (DCM) or dimethylformamide (DMF) consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a platinum wire quasireference electrode. The ferrocene/ferrocenium couple ($Fc/Fc^+$) was used as an internal standard and potentials are reported with respect to $Fc/Fc^+$ in nonaqueous solutions. High-purity argon was used for the deoxygenation of the cell at least 10 min prior to electrochemical measurements, and the solution was protected from air by a blanket of argon during the experiments. Mass spectra were acquired with a Voyager-DE$^{TM}$ PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded in reflectron and linear modes with an average of 50 shots. Indolin acrylic acid (IAA) (40 $mg\,mL^{-1}$ in methanol), 2,4-dinitrobenzene (DNB) (40 $mg\,mL^{-1}$ in acetonitrile), and Dithranol (1,8-dihydroxy-10*H*-anthracen-9-one; 20 $mg\,mL^{-1}$ in tetrahydrofuran) matrixes were used for **5**, **6**, and **7**, respectively. MALDI sample was prepared by mixing the complex (2 $mg\,mL^{-1}$ in tetrahydrofuran) with the matrix solution (1:10) 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. The second harmonic of Nd:YAG laser (Quantel Brillant) was used as the excitation light source with a pulse width of 4 ns and a repetition rate of 10 Hz. The experiment technique used in the measurements was the Z-scan technique.[46] In the Z-scan experiment, while sample was translated along *z* axis in the vicinity of the focal point of a 20 cm focal length lens, open-aperture signals were detected with a silicon detector. The concentrations of **6** and **7** were $1\times10^{-3}$ and $2\times10^{-3}$ M with a linear absorption coefficient of 2.54 and 1.94 $cm^{-1}$, respectively. All samples were placed in a quartz cell of 1 mm thickness and dimethyl sulfoxide was used as the solvent. As the samples were taken in a 1 mm cuvette, thin lens condition was satisfied.

**4-[2-(2*H*-1,2,3-Benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenoxy]phthalonitrile (3):** A mixture of **1** (2.24 g, 5 mmol) and **2** (0.87 g, 5 mmol) in dry DMF (25 mL) was stirred at 70–90 °C for 10 min and then the fine powder of dry $K_2CO_3$ (2.10 g, 15 mmol) was added portionwise over 1 h under an argon atmosphere. The reaction was then stirred for 12 h under an argon blanket. Then, the reaction mixture was poured into water (500 mL), and the precipitate formed was filtered, washed with water, and dried in air. The crude product was crystallized from ethanol. Product **3** is soluble in ethanol, methanol, $CHCl_3$, THF, DMF, and DMSO. Yield: 1.87 g (65%). M.p. 94–97 °C. IR (KBr disc): $\tilde{\nu}$ =3110–3008 (Ar-H), 2900–2840 ($-CH_3$), 2226 (-CN), 1594–1486 (-C=C-), 1250–1278 (Ar-O-C), 1495 and 1457 (Ar-H) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.72 (s 6 H), 1.85 (s 6 H), 6.42 (s 1 H), 6.75 (s 1 H), 6.76–7.00 (m 4 H), 7.23–7.43 (m 9 H), 7.66–7.84 (m 4 H) ppm. $C_{38}H_{31}N_5O$ (573.67): calcd. C 79.56, H 5.45, N 12.21; found 79.40, H 5.23, N 12.43.

**5-[2-(2*H*-1,2,3-Benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenoxy]-1,3-diiminoisoindoline (4):** To a solution of **3** (1.50 g, 2.61 mmol) in dry methanol (100 mL), was added sodium methoxide (0.082 g, 1.52 mmol). Anhydrous ammonia was bubbled through the solution under reflux. The course of the reaction was followed by IR spectroscopic monitoring of the C=N peak at 2226 $cm^{-1}$. After completion of the reaction, the ammonia inlet was closed, and the volume of the reaction mixture was reduced to 25 mL under reduced pressure. The mixture was precipitated with water (250 mL), and the solid was filtered off. The product was crystallized from methanol/acetone (1:5) to afford **4** as pale yellow crystals. Yield: 1.40 g (90%). M.p. 128–131 °C. IR (KBr disc): $\tilde{\nu}$ = 3500–3200 (NH), 3110–3004 (Ar-H), 2900–2840 ($-CH_3$), 1650 (=NH), 1600–1440 (-C=C-), 1253–1303 (Ar-O-C), 1495 and 1465 (Ar-H) $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.72 (s 6 H), 1.85 (s 6 H), 6.42 (s 1 H), 6.75 (s 1 H), 6.76–7.00 (m 4 H), 7.23–7.43 (m 9 H), 7.66–7.84 (m 4 H), 8.52 (br. 3 H) ppm. $C_{38}H_{34}N_6O$ (590.72): calcd. C 77.26, H 5.80, N 14.23; found C 77.51, H 5.62, N 14.35.

**[2,9,16,23-Tetrakis{2-(2*H*-benzo-1,2,3-triazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenoxy}phthalocyaninato]cobalt(II) (5):** A mixture of **3** (0.574 g, 1 mmol) and cobalt(III) acetate tetrahydrate (0.063 g, 0.25 mmol) or **3** (0.574 g, 1 mmol) and copper(II) acetate monohydrate (0.050 g, 0.25 mmol) in DMF (5 mL) was heated at reflux under an argon atmosphere for 24 h. After cooling to room temperature, ethanol (10 mL) was added, and the mixture was precipitated with water (250 mL). The green precipitate was filtered off and washed several times ethanol and acetone and dried in vacuo at 80 °C. The product is soluble in $CHCl_3$, $CH_2Cl_2$, DMF, DMSO, and THF. Yield: 0.410 g (70%, mixture of regioisomers). M.p. >300 °C. UV/Vis (THF): $\lambda$ (log $\varepsilon$) = 670 (4.46), 615 (4.12), 335 (4.31), (sh.) nm. IR (KBr pellet): $\tilde{\nu}$ = 30591, 1736, 1615, 1467, 1402, 1364, 1270, 1235, 1094, 958, 746, 700 $cm^{-1}$. $C_{152}H_{124}CoN_{20}O_4$ (2353.68): calcd. C 77.65, H 5.31, N 11.90; found C 76.45, H 5.43, N 12.21. MS (MALDI-TOF): *m*/*z* = $[M + H]^+$ 2352–2358 (because of isotopic distribution).

**[2,9,16,23-Tetrakis{2-(2*H*-benzo-1,2,3-triazol-2-yl)}-4,6-bis(2-phenylpropan-2-yl)(phenoxy)phthalocyaninato]copper(II) (6):** Synthesized by a procedure similar to that above for **5**. The product is soluble in $CHCl_3$, $CH_2Cl_2$, DMF, DMSO, and THF. Yield: 0.385 g (65%, mixture of regioisomers). M.p. >300 °C. UV/Vis (THF): $\lambda$ (log $\varepsilon$) = 680 (4.27), 615 (4.10), 355 (4.21) nm. IR (KBr pellet): $\tilde{\nu}$ = 3057, 2966, 1614, 1494, 1465, 1401, 1325, 1233, 1092, 950, 746, 700 $cm^{-1}$. $C_{152}H_{124}CuN_{20}O_4$ (2358.29): calcd. C 77.44, H 5.30, N 11.88; found C 76.98, H 5.16, N 12.11. MS (MALDI-TOF): 2356–2362 (because of isotopic distribution).

**Bis[tetrakis-2,9,16,23-{2-(2*H*-1,2,3-benzotriazol-2-yl)}-4,6-bis(2-phenylpropan-2-yl)phenoxy Phthalocyaninato]lutetium(III) (7):** A mixture of **4** (0.300 g, 0.51 mmol), lutetium acetate monohydrate (0.023 g, 0.063 mmol), and DBU (0.25 mL) was heated at reflux in *n*-octanol (3.0 mL) under an argon atmosphere for 12 h. The product was precipitated with methanol (50 mL) and filtered off. Then, the product was dissolved in THF and purified by silica-gel column chromatography (THF/methanol, 10:1). The dark green product was collected and precipitated in water, filtered off, and dried in vacuo at 80 °C. Yield: 0.074 g (25%). UV/Vis (THF): $\lambda$ (log $\varepsilon$) = 450 (4.41) (sh.), 615 (4.40), 685 (5.13) nm. IR (KBr pellet): $\tilde{\nu}$ = 3081, 3054, 3021, 2962, 2924, 2854, 1601, 1494, 1468, 1401, 1340, 1295, 1273, 1235, 1094, 1032, 940, 852, 747, 700 cm$^{-1}$. $C_{304}H_{248}LuN_{40}O_8$ (4764.45): calcd. C 76.64, H 5.25, N 11.76; found C 76.28, H 5.42, N 11.37. MS (MALDI-TOF): *m*/*z* = 4762–4772 $[M + H]^+$ (because of isotopic distribution).

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