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Large Two-Photon Absorption Cross Sections of Hemiporphyrazines in the Excited State: The Multiphoton Absorption Process of Hemiporphyrazines with Different Central Metals

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Abstract: A series of five hemiporphyrazines (Hps) with different coordinating central atoms (H₂, GeCl₂, InCl, Pt, Pb), and the acyclic derivative 1,3-bis-(6'-amino-4'-butoxy-2'-pyridylimino)-1,3-dihydroisindoline have been synthesized and their multiphoton absorption properties examined at the second harmonic frequency of the Nd:YAG laser in the nanosecond time regime. Metal-free and platinum Hps display saturation of optical transmittance within incident fluence values of 6 J cm⁻². Comparison with other similar molecular structures like phthalocyanines and related molecules shows that Hps are strong nonlinear absorbers. The experimental curves of nonlinear transmission at 532 nm have been fitted by means of a three-level model with the occurrence of simultaneous two-photon absorption from an excited state. In the sole case of the InCl complex we found that a five-level model is needed because of the participation of triplet states. Contrary to phthalocyanines, naphthalocyanines, and porphyrins, a heavy central atom does not improve the nonlinear absorption properties since a different excited states dynamic is involved. The large nonlinear absorption of Hps combined with the very small absorption in the visible spectral range makes these molecules a very interesting class of molecules for nonlinear optical applications.

Introduction

The research on new multiphoton absorption molecules for nonlinear optical applications like optical power limiting,¹ optical data storage,² microfabrication,^{2e,3} imaging,⁴ and photodynamic therapies⁵ is always looking for efficient processes with high nonlinear absorption cross sections. Multiphoton absorption can be obtained as simultaneous processes, like two

and three photon absorptions,⁶ or as sequential processes where one or more photons are absorbed from excited states which are highly populated during a laser pulse.^{7,8} In the last case one can observe very large optical responses due to the larger polarizability of excited states with respect to the ground state.^{7,9}

Hemiporphyrazines (Hps) are conjugated macrocycles with C_{2v} symmetry based on two cofacial pyridine rings and two

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cofacial isindoline units linked through four aza bridges.^{10,11} Similar to phthalocyanines (Pcs),¹² Hps ligands can coordinate a large number of central atoms and the syntheses of hemiporphyrinic complexes with H₂, Co, Ni, Cu, Zn, Fe, Mn, Pd, Pb, GeCl₂, VO, and InCl as central moieties have been reported.^{13–18} Due to the synthesis versatility¹⁹ Hps can be also obtained as polymers in the ladder configuration²⁰ or as axially bridged stacked systems.²¹ One of the most intriguing aspects that emerges from the analysis of the physicochemical properties of Hps is their strong structural resemblance with Pcs, but, contrary to these molecules, they show a nearly complete absence of absorptions in the visible and near-infrared spectrum. In fact, the presence in Hps of an extended aromatic ring with eighteen conjugated π -electrons and C_{2v} symmetry determines

transitions only in the near UV.^{21c,22,23} This feature combined with strong nonlinear absorption is appealing for example for the protection of optical sensors operating in the visible range from high intensity lasers. In fact, an optical power limiting device should possess high optical transmission in the rest state and very low nonlinear transmission in the activated state within the same spectral range.^{1,24}

The combination of optical and coordination properties of Hps has recently stimulated our interest toward Hps as photoactive materials for nonlinear optical (NLO) applications.^{18a} A previous study proved, for the first time, that an hemiporphyrinato indium chloride complex (HpInCl)^{18a} shows reverse saturable absorption (RSA),⁸ in the ns time regime. In analogy with the behavior of other conjugated macrocyclic complexes

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like Pcs,^{8f,24} porphyrins,^{8c,25} or naphthalocyanines,²⁶ such an NLO phenomenon was rationalized with a multiphoton absorption process which, in the lower intensity regime, was due to a stronger absorption of an excited triplet state.^{18a} Since the RSA dynamic depends on ligand structure,^{24d,f,g,25i,26g} irradiation conditions (laser wavelength^{24b,26b} and pulse duration^{25b,27}) and, more important, on the nature of central atom,^{8f,24e,26h} which can favor an intersystem crossing toward the triplet state, we have focused our attention toward the nonlinear absorption properties of a series of various Hps which differ for the nature of the coordinating central atoms. In particular, we have considered the synthesis of hemiporphyrinato dichlorogermanium (HpGeCl₂, **1**),¹⁶ metal-free 2(3),15(16)-bis-(3,5-di-*tert*-butyl-phenoxy)hemiporphyrazine [(*t*-Bu₂PhO)₂HpH₂, **2**],²³ 9,22-bis-(dihexyloxy)hemiporphyrinato platinum [(HexO)₂HpPt, **3**],²⁸ 9,22-bis-(dibutoxy) hemiporphyrinato chloroindium [(BuO)₂HpInCl, **4**],^{18a} and 9,22-bis-(dibutoxy) hemiporphyrinato lead [(BuO)₂HpPb, **5**] (see Chart 1), in order to determine the role of central atoms in the excited-state dynamics. The multiphoton absorption properties of the complexes **1–5** and the dynamics of their excited states under irradiation have been recorded using ns laser pulses at 532 nm because it was shown that these long pulses can also explore multiphoton absorptions from excited states with very large cross sections.^{7c}

Beside the closed forms of Hps **1–5**, the preparation of the open structure 1,3-bis-(6'-amino-4'-butoxy-2'-pyridylimino)-1,3-dihydroisindoline (Pyr₂Ind, **6**) has been also considered (see

Chart 2)^{20c,29} to verify how the conformational freedom, the reduction of the extent of π -electron conjugation, and the absence of a central metal influence the nonlinear absorption properties.

Experimental Section

Hemiporphyrinato Dichlorogermanium (1). Phthalonitrile and 2,6-diaminopyridine were refluxed in 1-chloronaphthalene according to the procedure reported by Kenney et al. to give the metal-free hemiporphyrazine.¹⁶ The latter was added to a quinoline solution of germanium tetrachloride and then refluxed adopting the conditions described in ref 16 for the production of **1**. Analytical data confirmed the formation of the dichlorogermanium complex HpGeCl₂ (**1**) as reported in ref 16. UV-vis (toluene), λ /nm (ϵ /M⁻¹ cm⁻¹): 315.5 (0.508 \times 10⁴), 364.5 (0.897 \times 10⁴), 384.5 (1.388 \times 10⁴), 408.0 (1.575 \times 10⁴). ¹³C-CP/MAS NMR, δ _C/ppm: 156.4 (C-5), 141.9 (C-4), 134.7 (C-7), 133.8 (C-3), 131.8, 127.1, 124.3, 122.4 (C-1/2/6).

2(3),15(16)-Bis-(3,5-di-*tert*-butyl-phenoxy)hemiporphyrazine (2).^{14c} A 2 g portion (2 \times 10⁻² mol) of 2,6-diaminopyridine and 6.6 g (2 \times 10⁻² mol) of 4-[(3,5-di-*tert*-butyl)-phenoxy]-1,2-benzenedicarbonitrile³⁰ were mixed in dry butanol (50 mL) and heated at 120 °C under N₂ atmosphere till the disappearance of gas evolution. The yellow precipitate (*t*-Bu₂PhO)₂HpH₂ (**2**) was washed with methanol and then dried. Yield: 2.4 g (2.8 \times 10⁻³ mol, 28%). UV-vis (toluene), λ /nm (ϵ /M⁻¹ cm⁻¹): 306.0 (0.982 \times 10⁴), 343.0 (0.766 \times 10⁴), 392.0 (0.436 \times 10⁴). IR (KBr), ν /cm⁻¹: 3448 (broad, strong), 2962 (broad, strong), 2934 (broad, strong), 2870 (broad, strong), 1674 (sharp, medium), 1585 (broad, strong), 1547 (sharp, medium). ¹H NMR (250 MHz, CDCl₃, Me₄Si), δ _H/ppm: 10.2 (s, 2H, NH pyrrole), 8.62, 8.57 (broad singlets, 4H, H-2, H-5), 7.97 (d, 2H, H-10), 7.32 (t, 4H, H-9, H-11), 7.16 (q, 2H, H-3), 6.60 (d, 2H, H-4'), 6.36 (q, 4H, H-2', H-2''), 1.3 (s, 36H, H-1'''). ¹³C NMR (60.9 MHz, CDCl₃, Me₄Si), δ _C/ppm: 173.5 (C-7, C-8), 157.3 (C-1'), 152.9 (C-4), 150.4 (C-3'), 140.3 (C-10), 135.7–133.4 (C-5, C-2), 131.1 (C-3), 128.1 (C-4'), 125.2–121.9 (C-9, C-11), 116.9 (C-1, C-6), 109.7 (C-2'), 35.3 (C-1''), 29.9 (C-1'''). MS (EI, 70 eV), *m/z*: 849.4 [M⁺], calcd. 848.5. Anal. Calcd. for C₅₄H₅₆N₈O₂, %: C, 76.39; H, 6.65; N, 13.20. Found: C, 75.87; H, 6.40; N, 12.91. Similar to phthalocyanines, the discrepancies between calculated and experimental values of the Hps elemental analysis are due to their high melting point, which determines uncomplete burning.

9,22-Bis-(dihexyloxy)hemiporphyrinato Platinum (3). The complex (HexO)₂HpPt (**3**) has been prepared upon reaction of 9,22-bis-(dihexyloxy)hemiporphyrazine^{14b} with platinum dichloride (PtCl₂) in excess taking DMF as solvent. The metal-free complex 9,22-bis-(dihexyloxy)hemiporphyrazine (320 mg, 0.5 mmol) was added with PtCl₂ (800 mg, 3 mmol) in 5 mL of dry DMF. The mixture was heated up to 140 °C for six hours. After cooling, water was added to precipitate the mixture. The solid was filtered and then washed with water and cold methanol to remove traces of residual solvent. Column chromatography on silica gel was performed using a mixture of chloroform and methanol (1%) as eluent to separate the metallated from the metal free complex in the solid. The first yellow fraction contained the metallated product. Chromatographic separation was checked by means of the spectral analysis of the outcoming fraction. Platinum hemiporphyrazine **3** appears as yellowish powder in the adopted experimental conditions of reaction and purification. Yield: 170 mg (0.2 mmol/40%). UV-vis (toluene), λ /nm (ϵ /M⁻¹ cm⁻¹): 396.0 (1.336 \times 10⁴), 422.0 (0.942 \times 10⁴), 450.5 (1.160 \times 10⁴), 479.5 (1.375 \times 10⁴). IR (KBr), ν /cm⁻¹: 3096 (broad, strong), 2951 (broad, strong), 2934 (broad,

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Chart 1. Hemiporphyrazinato Dichlorogermanium (HpGeCl₂, **1**), Metal-free 2(3),15(16)-Bis-(3,5-di-*tert*-butyl-phenoxy)hemiporphyrazine [(*t*Bu₂PhO)₂HpH₂, **2**], 9,22-bis-(dihexyloxy) Hemiporphyrazinato Platinum [(HexO)₂HpPt, **3**], 9,22-Bis-(dibutoxy)hemiporphyrazinato Chloroindium [(BuO)₂HpInCl, **4**], and 9,22-Bis-(dibutoxy)hemiporphyrazinato Lead [(BuO)₂HpPb, **5**]

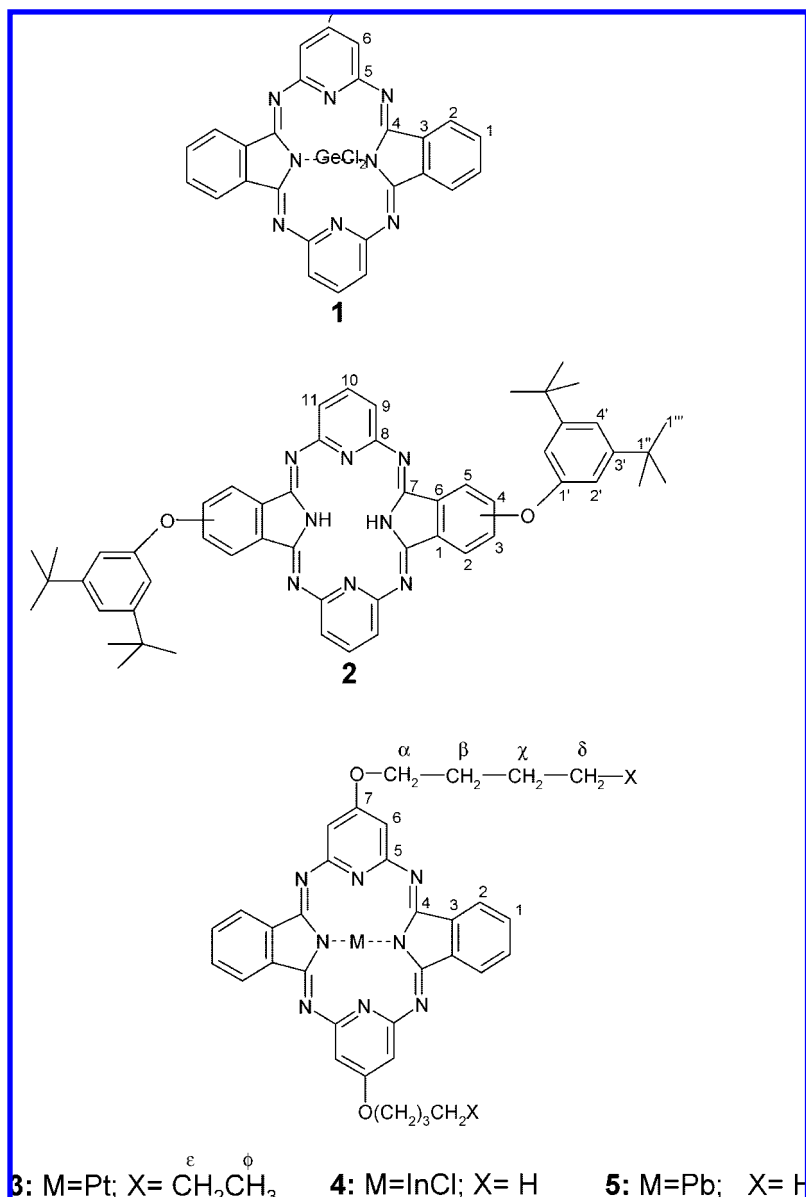
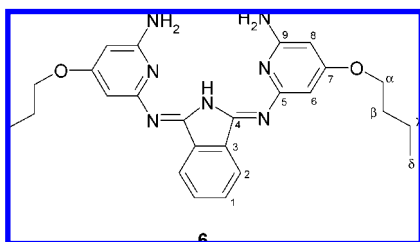


Chart 2.

Bis-(6'-amino-4'-butoxy-2'-pyridylimino)-1,3-dihydroisindoline (Pyr₂Ind, **6**)



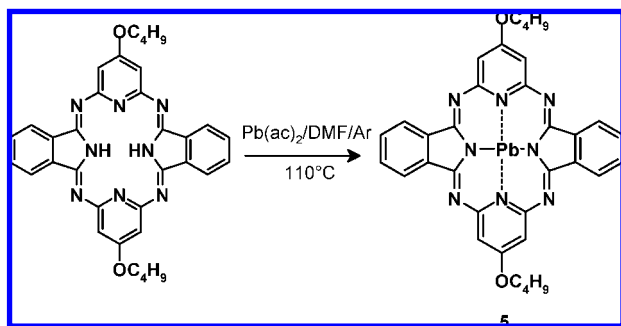
strong), 2851 (broad, strong), 1647 (sharp, medium), 1587 (broad, strong), 1545 (sharp, medium), 1468 (sharp, strong), 1427 (shoulder, medium), 1417 (shoulder, medium), 1370 (sharp, medium), 1321 (sharp, medium), 1217 (sharp, medium), 1198 (sharp, weak), 1107 (sharp, medium), 1051 (sharp, weak), 702 (sharp, strong). ¹H NMR (250 MHz, CDCl₃, Me₄Si), δ_H/ppm: 7.63 (m, 4H, H-2), 7.39 (m, 4H, H-1), 6.21 (s, 4H, H-6), 3.82 (t, 4H, H-α, *J* = 6.6 Hz), 1.71

(m, 4H, H-β), 1.34 (m, 12H, H-χ, H-δ, H-ε), 0.93 (t, 6H, H-φ, *J* = 6.6 Hz). ¹³C NMR (60.9 MHz, CDCl₃, Me₄Si), δ_C/ppm: 167.31 (C-7), 159.03 (C-5), 156.85 (C-4), 137.46 (C-3), 129.82 (C-1), 120.87 (C-2), 106.9 (C-6), 68.28 (C-α), 31.48 (C-β), 28.89 (C-χ), 25.43 (C-δ), 22.50 (C-ε), 13.96 (C-φ). MS (EI, 70 eV), *m/z*: 834.4 [M⁺], calcd. 833.3. Anal. Calcd. for C₃₈H₃₈N₈PtO₂, %: C, 54.74; H, 4.59; N, 13.44. Found: C, 53.98; H, 4.81; N, 12.88.

9,22-Bis-(dibutoxy)hemiporphyrazinato Chloroindium (4). The details of the synthesis of the indium complex (BuO)₂HpInCl (**4**) have been previously reported in ref 18a. UV-vis (toluene), λ/nm (ε/M⁻¹ cm⁻¹): 360.0 (1.559 × 10⁴), 379.0 (1.336 × 10⁴), 403.0 (0.779 × 10⁴).

9,22-Bis-(dibutoxy)hemiporphyrazinato Lead (5). The hemiporphyrazinato lead complex **5** was obtained by heating 9,22-bis-(dibutoxy)hemiporphyrazine^{18a} with lead(II) acetate (Pb(ac)₂) in excess (Scheme 1). A suspension of 290 mg (0.5 mmol) of metal free hemiporphyrazine and 650 mg (2 mmol) of Pb(ac)₂ in 4 mL dry DMF was heated at 110 °C for five hours. After cooling, water was added to precipitate the mixture. The solid was washed with water and cold methanol to remove DMF traces. After washing

Scheme 1. Synthesis of Compound 5



the solid was dried at 80 °C in vacuum. Yield: 250 mg (0.40 mmol, 80%) yellowish solid. Mass (EI, 70 eV), m/z : 791.1 [M⁺], 733 [M⁺ - C₄H₉], calcd 790.2. UV-vis (toluene), λ/nm ($\epsilon/M^{-1} \text{ cm}^{-1}$): 368.0 (1.519×10^4). ¹H NMR (CDCl₃); δ_H/ppm : 0.95 (t, 6H), 1.52 (m, 4H), 1.75 (m, 4H), 3.96 (t, 4H, OCH₂), 6.33 (4H, H-6), 7.58 (br, 4H, H-1), 7.80 (br, 4H, H-2). ¹³C NMR (CDCl₃); δ_C/ppm : 13.70 (C- δ), 19.14 (C- χ), 30.83 (C- β), 68.08 (C- α), 107.22 (C-6), 120.91 (C-2), 129.39 (C-1), 137.89 (C-3), 155.7 (C-4), 157.19 (C-5), 167.49 (C-7).

1,3-Bis-(6'-amino-4'-butoxy-2'-pyridylimino)-1,3-dihydroisoindoline (6). A mixture of 1.45 g (10^{-2} moles) of 1,3-dihydro-1,3-diiminoindoline and 7.24 g (4×10^{-2} moles) of 4-butoxy-2,6-diaminopyridine^{14b,c,31} were dissolved and stirred in absolute methanol (50 mL) under N₂ flux until no development of NH₃ was observed. The precipitate Pyr₂Ind (6) was filtered and successively washed with methanol. The product was then dissolved in acetone and chromatographed in this solvent on silica gel. Yield: 3.17 g (6.7×10^{-3} moles, 67%). UV-vis (toluene), λ/nm ($\epsilon/M^{-1} \text{ cm}^{-1}$): 401.0 (0.702×10^4), 423.0 (0.657×10^4), 455.5 (0.296×10^4). IR (KBr), ν/cm^{-1} : 3435 (broad, strong), 3365 (broad, strong), 3306 (broad, strong), 2959 (broad, strong), 2934 (broad, strong), 2874 (broad, strong), 1643 (sharp, medium), 1597 (broad, strong), 1566 (sharp, medium), 1443 (shoulder, medium), 1379 (sharp, medium), 1300 (sharp, medium), 1215 (sharp, medium), 1194 (sharp, medium), 825, 704 (sharp, strong). ¹H NMR (250 MHz, CDCl₃, Me₄Si), δ_H/ppm : 13.2 (s, 1H, NH pyrrole), 7.53 (m, 2H, H-1), 7.95 (m, 2H, H-2), 6.36 (d, 2H, H-6), 5.75 (d, 2H, H-8), 4.59 (s, 4H, NH₂), 3.91 (t, 4H, H- α , $J = 7.5$ Hz), 1.68 (m, 4H, H- β , H- γ), 0.89 (t, 6H, H- δ , $J = 7.3$ Hz). ¹³C NMR (60.9 MHz, DMSO-*d*₆, Me₄Si), δ_C/ppm : 131.8 (C-1), 122.14 (C-2), 135.05 (C-3), 151.31 (C-4), 159.80 (C-5), 98.93 (C-6), 167.47 (C-7), 90.37 (C-8), 160.07 (C-9), 67.07 (C- α), 30.55 (C- β), 18.70 (C- γ), 13.64 (C- δ). MS (EI, 70 eV), m/z : 474.1 [M⁺], 430.1 [M⁺ - C₃H₇], calcd. 473.2. Anal. Calcd for C₂₆H₃₁N₇O₂, %: C, 65.94; H, 6.59; N, 20.70. Found: C, 66.07; H, 6.40; N, 20.10.

Nonlinear Optical Transmission Measurements. The multiphoton absorption properties of **1–6** were obtained with nonlinear optical transmission measurements. The measurements were carried out with 9 ns pulses at 532 nm of a doubled Nd:YAG laser (Quanta YG980E), at 1 Hz in an open-aperture configuration.^{18a,24g} Transmitted energies were measured for every single pulse with a pyroelectric detector (Scientech mod. SPHD25) and the energy of the reference beam was measured with a calibrated photodiode. The intensity of the incident pulses was controlled with a $\lambda/2$ waveplate and a polarizing cube beam-splitter. The illuminated area on the sample was $5 \times 10^{-2} \text{ cm}^2$. The measurements were carried out using 2 mm glass cells. Linear optical spectra of the solutions

were recorded with a Varian Cary 5 UV-vis spectrophotometer before and after the measurement of the nonlinear optical transmission in order to evaluate possible photodegradation.

Pump and Probe Experiments. Pump and probe experiments were performed to obtain the lifetime and spectral properties of the Hps excited states, which are responsible for the nonlinear optical behavior. The nanosecond laser pulses used for the nonlinear transmission measurements were used as pump while the probing of the absorption kinetic at different wavelengths was carried out on a microsecond time scale with nanosecond resolution. A Xenon lamp was used as a source for the probe and 1-GHz digital oscilloscope (LeCroy LC564A) was employed to record the transient signals which were detected by a Jobin-Yvon Horiba TRIAX 320 spectrometer equipped with an Hamamatsu phototube (R2257).

Results and Discussions

Linear Optical Properties. The values of the molar extinction coefficient (ϵ) in the UV-vis spectral region for compounds **1–6** are presented in Figure 1.

Hps **1–5** and Pyr₂Ind (**6**) in toluene display moderate absorption being $\epsilon < 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in the near UV range, and this feature imparts a yellowish color to the solutions of these systems.^{13,22} For wavelengths longer than 500 nm Hps and Pyr₂Ind spectra become practically flat with no relevant absorption (see Figure 1), the sole exception being (HexO)₂HpPt (**3**), which also shows a bathochromic shift of its absorption bands with respect to the other Hps here considered. A molecular distortion could be the origin of this different absorption spectrum, but further analyses are needed for understanding this behavior. Well-resolved peaks are observed in the absorption spectrum of some complexes and their origin has been found to be related to various $\pi \rightarrow \pi^*$ transitions, from the HOMO and lower molecular orbitals to the LUMO, and localized on the hemiporphyrine macrocycle.²³

Multiphoton Absorption Properties. The nonlinear optical properties of hemiporphyrines **1–5** and the open structure Pyr₂Ind (**6**) have been determined using nanosecond laser pulses at 532 nm. The nonlinear transmittance (T_{532}) for the toluene solutions of compounds **1–6** has been recorded as a function of the incident fluence (F_{in}) within the broad range $0 < F_{in} < 6 \text{ J cm}^{-2}$ (Figure 2). For a direct comparison of the different nonlinear optical behaviors of Hps **1–5** and Pyr₂Ind (**6**) we have plotted in the same figure the data for those Hps solutions having the same value of linear transmittance [$T_0(532) = 0.96$ and 0.83 in parts a and b of Figure 2, respectively].

All species under investigation behave as reverse saturable absorbers^{8a–d} at 532 nm for nanosecond laser pulses in the investigated fluence range, since their transmission decreases at larger fluences.

In Table 1 the values of limiting threshold $F_{lim}(532)$, defined as the fluence value at which the nonlinear transmittance is half the value of the linear transmittance $T_0(532)$, and the values of molar extinction coefficient at 532 nm [$\epsilon(532)$] are listed for compounds **1–6**.

The lowest values of $F_{lim}(532)$ are found around 0.5 J cm^{-2} and are associated to the nonlinear optical behavior of those hemiporphyrine complexes which reach transmission saturation for $F_{in}(532) < 5 \text{ J cm}^{-2}$, that is, (tBu₂PhO)₂HpH₂ (**2**) and (HexO)₂HpPt (**3**) (Figure 2). The indium chloride complex **4** shows a value of $F_{lim}(532) = 1.85 \text{ J cm}^{-2}$, which is intermediate,^{18a} whereas for HpGeCl₂ (**1**) and PyrInd (**6**) $F_{lim}(532)$ could be only estimated because in the adopted experimental conditions the highest value of $F_{in}(532)$ did not permit

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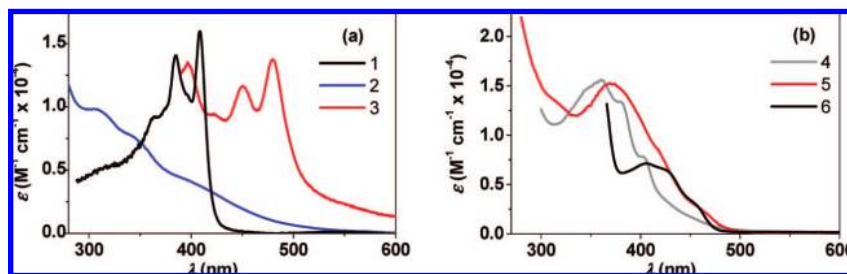


Figure 1. Molar extinction coefficient (ϵ) values in the UV-vis range for the toluene solutions of (a) HpGeCl_2 (1), $(\text{rBu}_2\text{PhO})_2\text{HpH}_2$ (2), $(\text{HexO})_2\text{HpPt}$ (3), (b) $(\text{BuO})_2\text{HpInCl}$ (4), $(\text{BuO})_2\text{HpPb}$ (5), and Pyr_2Ind (6).

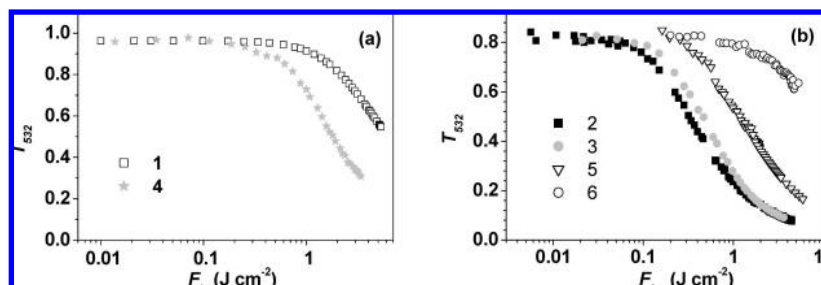


Figure 2. Nonlinear transmission at 532 nm (T_{532}) of (a) HpGeCl_2 (1), $(\text{BuO})_2\text{HpInCl}$ (4), (b) $(\text{rBu}_2\text{PhO})_2\text{HpH}_2$ (2), $(\text{HexO})_2\text{HpPt}$ (3), $(\text{BuO})_2\text{HpPb}$ (5), and Pyr_2Ind (6) upon increasing incident fluence (F_{in}). Linear transmittance at 532 nm ($T_0(532)$) is 0.96 for complexes 1 and 4 and 0.83 for compounds 2, 3, 5, and 6.

Table 1. Values of Ground-State Absorption Cross-Section at 532 nm [$\sigma_0(532)$], Molar Extinction Coefficient at 532 nm [$\epsilon(532)$], and Limiting Threshold at 532 nm [$F_{\text{lim}}(532)$] for the Toluene Solutions of Compounds 1–6

compound	$\sigma_0(532)$ (cm^2)	$\epsilon(532)$ (M^{-1} cm^{-1})	$F_{\text{lim}}(532)$ (J cm^{-2})
HpGeCl_2 (1)	11.8×10^{-20}	31	>5.4
$(\text{rBu}_2\text{PhO})_2\text{HpH}_2$ (2)	118.5×10^{-20}	310	0.45
$(\text{HexO})_2\text{HpPt}$ (3)	1070.9×10^{-20}	2801	0.60
$(\text{BuO})_2\text{HpInCl}$ (4)	101.3×10^{-20}	265	1.85
$(\text{BuO})_2\text{HpPb}$ (5)	6.1×10^{-20}	16	1.65
Pyr_2Ind (6)	64.6×10^{-20}	169	>5.6

us to reach the lower transmission levels because of the damage of cuvettes and focusing optics at larger fluences. For optical power limiting purposes a lower value of F_{lim} means a better photoactive material.^{1a,24b,32–34} In this framework Hps 2 and 3 are the best examples among compounds 1–6.

A comparison with the multiphoton absorption properties of similar molecules like phthalocyanines and porphyrins can be obtained considering that the nonlinear absorption of these systems derives from a one photon absorption from an excited state. Similarly, one can assume that the saturation of the nonlinear transmission (T_{min}), in particular in the case of the metal-free complex 2 and platinum hemiporphyrazine 3, can derive from an effective one-photon absorption

from a completely populated excited state, although later we will find that the excited states dynamic of Hps is different. We can obtain a cross section for the effective one-photon absorption simply by^{8d}

$$\sigma'(\lambda) = \ln[1/T_{\text{min}}(\lambda)]/NI \quad (1)$$

where N is the concentration of the molecules in solution (in cm^{-3}) and l the cell optical path (in cm).

In the case of hemiporphyrazines 2 and 3, $N = 7.3 \times 10^{17} \text{ cm}^{-3}$ (2) and $9.0 \times 10^{16} \text{ cm}^{-3}$ (3), and, since $T_{\text{min}}(532) = 0.08$ (2, 3) (see Figures 6 and 7) and $l = 0.2 \text{ cm}$, one finds $\sigma'(532) = 1.73 \times 10^{-17} \text{ cm}^2$ (2) and $14.0 \times 10^{-17} \text{ cm}^2$ (3). A figure of merit to compare the multiphoton activity of molecules with a one-photon excited-state absorption is obtained with the ratio $\kappa = \sigma'/\sigma_0$ where σ_0 is the ground-state absorption cross-section at the chosen wavelength of analysis. In the case of Hps 2 and 3, one obtains $\kappa = 14.4$ and 13.1, respectively, with $\sigma_0 = 1.2 \times 10^{-18}$ (2) and 10.7×10^{-18} (3) cm^2 . One observes that the similarity of κ values indicates that inserting a coordinating central atom does not considerably affect the nonlinear behavior of this type of complexes. A comparison of the κ values of Hps with those obtained for other classes of molecular nonlinear absorbers like phthalocyanines ($1 < \kappa < 34$),^{8d,24e} porphyrins

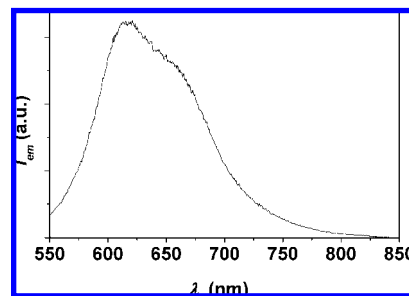


Figure 3. Emission spectrum of $(\text{BuO})_2\text{HpInCl}$ (4) in toluene. Excitation wavelength (λ_{exc}), 532 nm; concentration (C), $9.5 \times 10^{-4} \text{ M}$.

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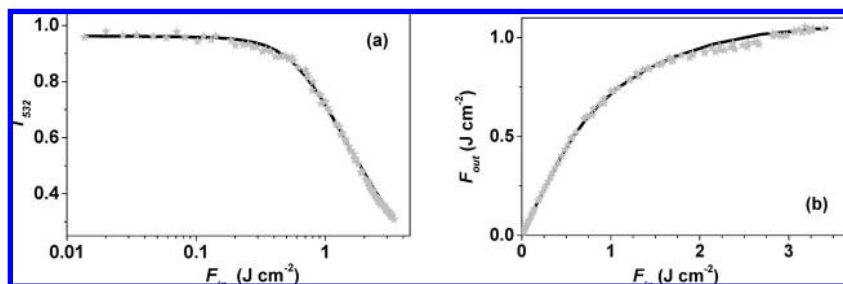


Figure 4. Plots of (a) nonlinear transmission vs incident fluence (T_{532} vs F_{in}) and (b) transmitted fluence (F_{out}) vs F_{in} for $(\text{BuO})_2\text{HpInCl}$ (**4**) at 532 nm. Fit (continuous line) of the experimental points (open circles) has been obtained with the multiphoton absorption model depicted in Figure 5.

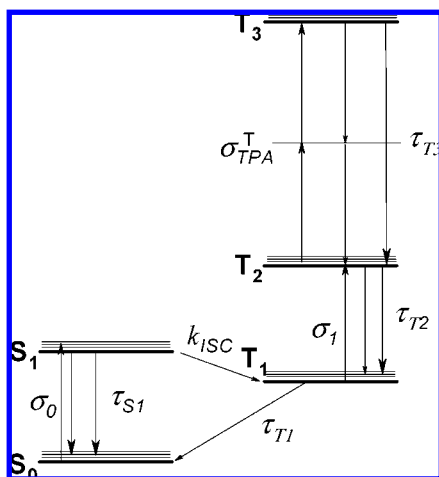


Figure 5. Model for the excited-state dynamics of $(\text{BuO})_2\text{HpInCl}$ (**4**) with a two-photon absorption from an excited triplet state.

($2 < \kappa < 35$),^{25c,d,g,35} and also C_{60} ($\kappa < 5$)^{8f} at 532 nm, for ns pulses, indicates that Hps represent a very effective class of multiphoton absorber materials.

Model for Nonlinear Optical Absorption Processes. The knowledge of F_{lim} (Table 1) or κ for compounds **1–6** does not give any insight into the actual mechanism of their nonlinear absorption. In a previous work, the lower fluences nonlinear transmission behavior of the complex $(\text{BuO})_2\text{HpInCl}$ (**4**) at 532 nm was obtained with a model in which one photon is absorbed from the ground-state and a second one from an excited triplet state with absorption cross-section of $1.6 \times 10^{-16} \text{ cm}^2$.^{18a} The activity of the excited triplet state in the nonlinear absorption process of **4** was confirmed with a pump and probe experiment which determined a value longer than 100 ns for the lifetime of an absorbing excited state.^{18a} We also observe a well-defined fluorescence emission (see Figure 3), in the broad range 550–825 nm, with a lifetime faster than the resolution of the pump and probe experiments with ns pulses. Although the observed large Stokes shift could suggest a phosphorescence emission, its lifetime and its intensity independence from the presence of oxygen point to a normal fluorescence emission.

The proposed model^{18a} proved to be valid for the fitting of the nonlinear transmission profile of $(\text{BuO})_2\text{HpInCl}$ (**4**) when $F_{in} < 0.9 \text{ J cm}^{-2}$, in correspondence of which small variations of the transmittance are observed (Figure 2). The same model could not fit the larger changes that occurred when $F_{in} > 1 \text{ J cm}^{-2}$. Therefore, an extension of that model is here proposed. The fast decreasing transmittance for $F_{in} > 1 \text{ J cm}^{-2}$ suggests that other linear or nonlinear absorptions occur from the populated states, namely the singlet and triplet states. We considered many possibilities among linear and nonlinear

excitations from these states and the simplest model which allowed a good fitting in the whole range of fluences (see Figure 4) considers a simultaneous absorption of two photons from the excited triplet state (see Figure 5). The good fitting can be seen in Figure 4, panels a and b, which show the same experimental data. In Figure 4a the transmittance $T (= F_{out}/F_{in})$ is plotted against the logarithm of F_{in} , whereas in Figure 4b F_{out} is directly plotted against F_{in} on a linear scale. The first plot gives more evidence to the low fluence regime ($F_{in} < 0.7 \text{ J cm}^{-2}$) in correspondence of the onset of NLO behavior of Hp **4**, whereas the second one shows better the highest fluence regime. Therefore, the two figures show that the experimental data are well-fitted by the model at all the explored fluences.

The differential equations which have been numerically solved³³ for the calculation of the temporal dependent populations are:

$$\frac{dN_{S0}}{dt} = -\sigma_0 N_{S0} I_{in} + \sigma_0 N_{S1} I_{in} + \frac{N_{S1}}{\tau_{S1}} + \frac{N_{T1}}{\tau_{T1}} \quad (2a)$$

$$\frac{dN_{S1}}{dt} = \sigma_0 N_{S0} I_{in} - \sigma_0 N_{S1} I_{in} - \frac{N_{S1}}{\tau_{S1}} - k_{ISC} N_{S1} \quad (2b)$$

$$\frac{dN_{T1}}{dt} = k_{ISC} N_{S1} - \sigma_1 N_{T1} I_{in} + \sigma_1 N_{T2} I_{in} - \frac{N_{T1}}{\tau_{T1}} + \frac{N_{T2}}{\tau_{T2}} \quad (2c)$$

$$\frac{dN_{T2}}{dt} = \sigma_1 N_{T1} I_{in} - \sigma_1 N_{T2} I_{in} - \frac{N_{T2}}{\tau_{T2}} - \sigma_{TPA}^T N_{T2} I_{in}^2 + \sigma_{TPA}^T N_{T3} I_{in}^2 + \frac{N_{T3}}{\tau_{T3}} \quad (2d)$$

$$\frac{dN_{T3}}{dt} = \sigma_{TPA}^T N_{T2} I_{in}^2 - \sigma_{TPA}^T N_{T3} I_{in}^2 - \frac{N_{T3}}{\tau_{T3}} \quad (2e)$$

In eqs 2 N_i represent population densities (see Figure 5 for the different levels), σ_i is the absorption cross sections for one- and two-photon processes, k_{ISC} is the intersystem crossing rate constant, τ_i is relaxation times, and I_{in} is the input intensity of the laser pulse as $\text{phot cm}^{-2} \text{ s}^{-1}$. Fitting of the data required the optimization of σ_1 , σ_{TPA}^T , the intersystem crossing k_{ISC} and the excited states lifetimes (see Figure 5). Although many parameters are involved in the fitting, confident bounds to the parameter values do not allow many possibilities. Fitting of the experimental curve of Figure 4 has been achieved with the following parameter values: $\sigma_1 = 3.9 \times 10^{-18} \text{ cm}^2$, $\sigma_{TPA}^T = 2.56 \times 10^{-42} \text{ cm}^4 \text{ s phot}^{-1} \text{ mol}^{-1}$, $k_{ISC} = 5.0 \times 10^8 \text{ s}^{-1}$, $\tau_{S1} = 1.1 \times 10^{-9} \text{ s}$, $\tau_{T1} = 2.0 \times 10^{-6} \text{ s}$, $\tau_{T2} = 1.2 \times 10^{-10} \text{ s}$, $\tau_{T3} = 1.6 \times 10^{-13} \text{ s}$. The value of linear absorption cross section at 532 nm $\sigma_0(532) = 1.0 \times 10^{-18} \text{ cm}^2$ was obtained from the

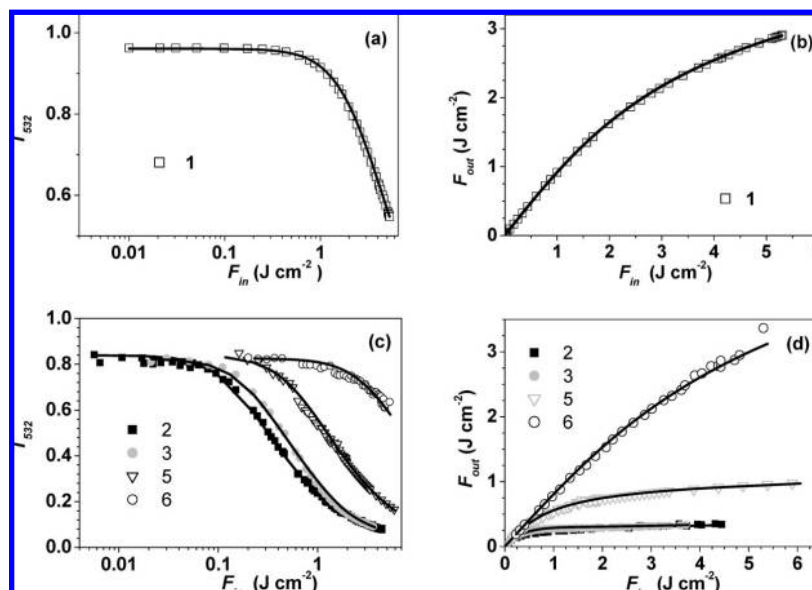


Figure 6. Fitting of T_{532} vs $\log(F_{in})$ (a,c) and F_{out} vs F_{in} (b,d) for HpGeCl_2 (1) (a,b) and $(t\text{Bu}_2\text{PhO})_2\text{HpH}_2$ (2), $(\text{HexO})_2\text{HpPt}$ (3), $(\text{BuO})_2\text{HpPb}$ (5), and Pyr_2Ind (6) (c,d) with the multiphoton absorption model shown in Figure 7 using parameter values reported in Table 2.

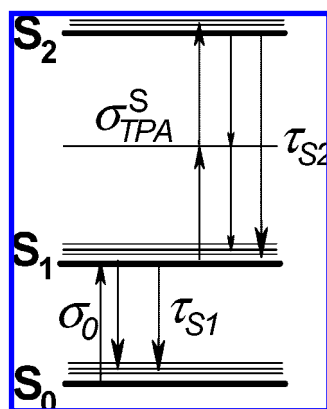


Figure 7. Model for the excited-state dynamics of hemiporphyrines 1–3, 5, and the open structure 6. σ_{TPA}^S and τ_{S2} denote the simultaneous two-photon absorption cross-section for the transition $S_1 \rightarrow S_2$ and the lifetime of the second excited singlet state S_2 , respectively.

linear spectrum (Figure 1). We also recall that the model fitting takes into account the spatial (almost top hat) and time (Gaussian) profiles of the laser pulses used for the experiments. One can observe that the absorption cross section for the simultaneous absorption of two photons from excited state, σ_{TPA}^S , has a very large value, which is four to five orders of magnitude larger than corresponding values usually observed for two-photon absorption processes from the ground state. This is characteristic of nonlinear processes which start from excited states since, as recalled above, excited states are very polarizable states and they can show very large optical responses.⁷

A much more simple model can be used for the fitting of the nonlinear transmittance data of the other compounds HpGeCl_2 (1), $(t\text{Bu}_2\text{PhO})_2\text{HpH}_2$ (2), $(\text{HexO})_2\text{HpPt}$ (3), $(\text{BuO})_2\text{HpPb}$ (5) and Pyr_2Ind (6) (Figures 6) since, different from hemiporphyrine 4, one can exclude, for these molecules, the presence of long-lived excited states ($\tau > 10^{-8}$ s). In fact, pump and probe experiments did not show any transient signal in the whole visible range (400–750 nm). Since a one photon excitation is found at low fluences, a decreasing transmittance at larger fluences indicates that a linear or a nonlinear absorption from

Table 2. Final Values of σ_{TPA}^S , τ_{S1} , and τ_{S2} for the NLO Transmission Curves Fittings (Figure 6)

compound	σ_{TPA}^S (532 nm) ($\text{cm}^2 \text{ s phot}^{-1} \text{ mol}^{-1}$)	τ_{S1} (s)	τ_{S2} (s)
HpGeCl_2 (1)	0.2×10^{-42}	1.3×10^{-10}	2.0×10^{-14}
$(t\text{Bu}_2\text{PhO})_2\text{HpH}_2$ (2)	45.2×10^{-42}	3.7×10^{-11}	7.9×10^{-13}
$(\text{HexO})_2\text{HpPt}$ (3)	289.0×10^{-42}	2.5×10^{-12}	2.4×10^{-14}
$(\text{BuO})_2\text{HpPb}$ (5)	57.8×10^{-42}	1.8×10^{-12}	2.5×10^{-14}
Pyr_2Ind (6)	0.09×10^{-42}	3.05×10^{-11}	2.0×10^{-14}

excited-state occurs. Considering a linear absorption from the first excited-state does not allow a fit of the experimental data, a very good fitting (Figure 6) can be obtained with a simultaneous two-photon absorption from this state. Alternative models, like a sequential two-photon absorption from this state, seem less probable because in this case one should populate a very excited-state which usually has short lifetimes and are not easily populated by long pulses like nanosecond pulses. Furthermore, more parameters, which are poorly characterized, should be included in the models.

The population dynamics of the model reported in Figure 7 were obtained with the following rate equations which have been numerically solved:³³

$$\frac{dN_{S0}}{dt} = -\sigma_0 N_{S0} I_{in} + \sigma_0 N_{S1} I_{in} + \frac{N_{S1}}{\tau_{S1}} \quad (3a)$$

$$\frac{dN_{S1}}{dt} = \sigma_0 N_{S0} I_{in} - \sigma_0 N_{S1} I_{in} - \frac{N_{S1}}{\tau_{S1}} - \sigma_{\text{TPA}}^S N_{S1} I_{in}^2 + \sigma_{\text{TPA}}^S N_{S2} I_{in}^2 + \frac{N_{S2}}{\tau_{S2}} \quad (3b)$$

$$\frac{dN_{S2}}{dt} = \sigma_{\text{TPA}}^S N_{S1} I_{in}^2 - \sigma_{\text{TPA}}^S N_{S2} I_{in}^2 - \frac{N_{S2}}{\tau_{S2}} \quad (3c)$$

with symbols already introduced after eqs 2. The analysis of the nonlinear transmission curves required the evaluation of only three parameters (σ_{TPA}^S , τ_{S1} , and τ_{S2}) which are reported in Table 2. One finds that the first two parameters are particularly important for the fitting.

One observes that the relaxation of the first excited singlet state is very similar for all compounds except for **1** for which it is one order of magnitude longer. Therefore, the parameter which determines the different nonlinear absorption of the molecules is, in particular, the two-photon absorption cross section from the excited singlet state. From the comparison of $\sigma_{\text{TPA}}^{\text{S}}$ values in Table 2 it results that metal free **2**, Pt **3**, and Pb **5** Hps display the largest values ($> 30 \times 10^{-42} \text{ cm}^4 \text{ s phot}^{-1} \text{ mol}^{-1}$). The different behavior of the open structure can be understood as a consequence of its lower electronic conjugation. For HpGeCl_2 (**1**) we observe that the lack of any peripheral substituent might determine stronger interaction with other molecules.³⁴ This phenomenon produces a faster decay of the first excited state (see Table 2) and, therefore, a less efficient simultaneous two-photon absorption from this state. Similarly to the InCl complex, one finds two-photon absorption cross sections which are an order of magnitude larger than those observed for ground-state two-photon absorption processes.⁷

The nonlinear transmission data of $(\text{BuO})_2\text{HpInCl}$ (**4**) cannot be properly fitted both at high and low fluences with the simpler model valid for all other Hps, because it does not include an intermediate long-lived excited state. This is in accordance with the presence of an absorbing excited triplet state for **4**, as it was verified with a pump and probe experiment, although the nonlinear absorption of the InCl complex is not like, for example, that of the analogue Pc complex^{8f} for which the linear absorption of the triplet state explains the whole nonlinear regime. The experimental evidence of the absence of long-lived triplet states for the other Hps complexes shows that Hps behave differently than similar systems like Pcs^{24a,b,35} and the reason could be found in different excited-state structures. Correlated electronic calculations, which are beyond the scope of the present paper, could address this behavior.

The models describing the excited-state population dynamics and multiphoton absorption of Hps are, however, substantially different from those of Pcs, their analogues, and C_{60} which show, in the nanosecond time regime, a one-photon absorption from an excited triplet state. In the case of Hps the simultaneous absorption of two photons from an excited state with very large cross sections renders these systems particularly interesting for photonic applications.

Conclusions

The synthesis of various hemiporphyrazines with a different central atom pattern of peripheral substitution and extent of

electronic conjugation has been carried out. Hemiporphyrazinato dichlorogermanium (HpGeCl_2 , **1**), metal-free 2(3),15(16)-bis-(3,5-di-*tert*-butyl-phenoxy)hemiporphyrazine [$(t\text{Bu}_2\text{PhO})_2\text{HpH}_2$, **2**], 9,22-bis-(dihexyloxy)hemiporphyrazinato platinum [$(\text{HexO})_2\text{HpPt}$, **3**], 9,22-bis-(dibutoxy) hemiporphyrazinato chloroindium [$(\text{BuO})_2\text{HpInCl}$, **4**], 9,22-bis-(dibutoxy) hemiporphyrazinato lead [$(\text{BuO})_2\text{HpPb}$, **5**] and 1,3-bis-(6'-amino-4'-butoxy-2'-pyridylimino)-1,3-dihydroisoindoline (Pyr_2Ind , **6**) with acyclic structure have been prepared. Compounds **1–6** have linear absorption in the near UV without relevant transitions at wavelengths longer than 500 nm. Their multiphoton absorption properties have been recorded using nanosecond laser pulses at 532 nm, and comparison with other multiphoton absorbing molecules like phthalocyanines or porphyrins have shown that Hps are very good nonlinear absorbers. The nonlinear transmission curves have been fitted with two different models for the dynamics of the excited states. We found that simultaneous two-photon absorption from an excited-state must be considered in order to model the high fluence region for all compounds. In the sole case of $(\text{BuO})_2\text{HpInCl}$ (**4**) the triplet manifold is involved, whereas the singlet manifold has to be considered in all the other cases. Confirmation of this behavior has been obtained from pump and probe measurements which show that only in the case of the InCl complex a long-lived excited state is formed. Very large values of cross section for a two-photon absorption process from an excited state were found for the metal free, platinum, and lead complexes $(t\text{Bu}_2\text{PhO})_2\text{HpH}_2$ (**2**), $(\text{HexO})_2\text{HpPt}$ (**3**), and $(\text{BuO})_2\text{HpPb}$ (**5**). The nonlinear absorption behavior was found, therefore, to be different from other similar systems like phthalocyanines and analogue molecules and can be considered another interesting class of molecules for photonic applications.

Acknowledgment. D.D., V.A., and M.M. thank the Italian Ministry of Universities and Research for funding (PRIN 2006, prot. 2006034372 and Fibr RBIN04HC3S) and Simone Crivellaro and Gabriele Marcolongo for technical help.

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JA802678U