

Investigation of relationship between chemical structures and optical limiting properties of pentaazadentat porphyrin-like metal complexes

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ABSTRACT

The optical limiting performances of nine asymmetric pentaazadentate porphyrin-like metal complexes ([(R-APPC)M]Cl_n) have been measured at 532nm with nanosecond pulses. In a *f*/38 geometry, with sample transmission of 0.51 ~ 0.80 in a 2 mm cell, the limiting thresholds for these complexes were 1.4 ~ 150.0 mJ/cm². The throughputs of these complexes were limited to 0.31 ~ 1.42 J/cm² for incident fluences as high as 3.5 J/cm². The limiting throughput was strongly influenced by the nature of the ligand and metal ions. Lower bounds for the ratio of triplet excited-state to ground state absorption cross sections have been estimated at 2.3 ~ 5.7. The lower limiting thresholds, lower limiting throughputs, as well as the ease of modification of the ligands and variation of the metal ions, make these complexes promising candidates for optical power limiters.

Keywords: asymmetric pentaazadentate porphyrin-like metal complexes, reverse saturable absorption (RSA), optical limiting, limiting threshold, limiting throughput, triplet excited-state, absorption cross section

1. INTRODUCTION

With the development of lasers and other high-intensity visible-light sources, the need for passive optical limiters to protect sensors and human eyes from intense optical beam has generated much interest in the development of new nonlinear optical materials and devices. In recent years, organic nonlinear optical materials^{1,2} have been studied because of their large nonlinearities, inherently fast response times, broadband spectral response and ease of processing and synthesis. Limiters based on nonlinear absorption have been reported using diphenyl polyenes,³ indanthrone dyes,⁴ metallophthalocyanines,⁵⁻¹⁰ metalloporphyrin,^{11,12} fullerenes,¹³ and some organometallic compounds.¹⁴ Among these materials, metallophthalocyanines and metallonaphthalocyanines were especially attractive because of their relatively low linear absorption and high ratios of excited state to ground state absorption cross sections (S_e/S_g) in the 450~600 nm region. The use of these complexes is limited,

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however, by their relatively high linear absorption outside of the 450~600 nm region and, in some cases, by the low quantum yields of their triplet excited states.

A related class of complexes are the asymmetric pentaazadentate porphyrin-like complexes $[(R-APPC)M]Cl_n$,^{15,16} examples of which are shown in Figure 1. These complexes have two-dimensional delocalized electronic systems and exhibit strong third-order nonlinearities like the metallophthalocyanines and metallonaphthalocyanines. However, unlike metallophthalocyanines and metallonaphthalocyanines, the ring structures of these complexes can be readily modified so that a more extended conjugated system (18~26 π -electron) can be obtained. Moreover, the large core size of the ligand provides a very stable coordination environment for large cations, therefore the choices for the metal ions are greatly expanded and a near coplanar configuration can be formed. Such structural modifications should allow $[(R-APPC)M]Cl_n$ complexes with optimal photophysical properties for a variety of applications to be developed.

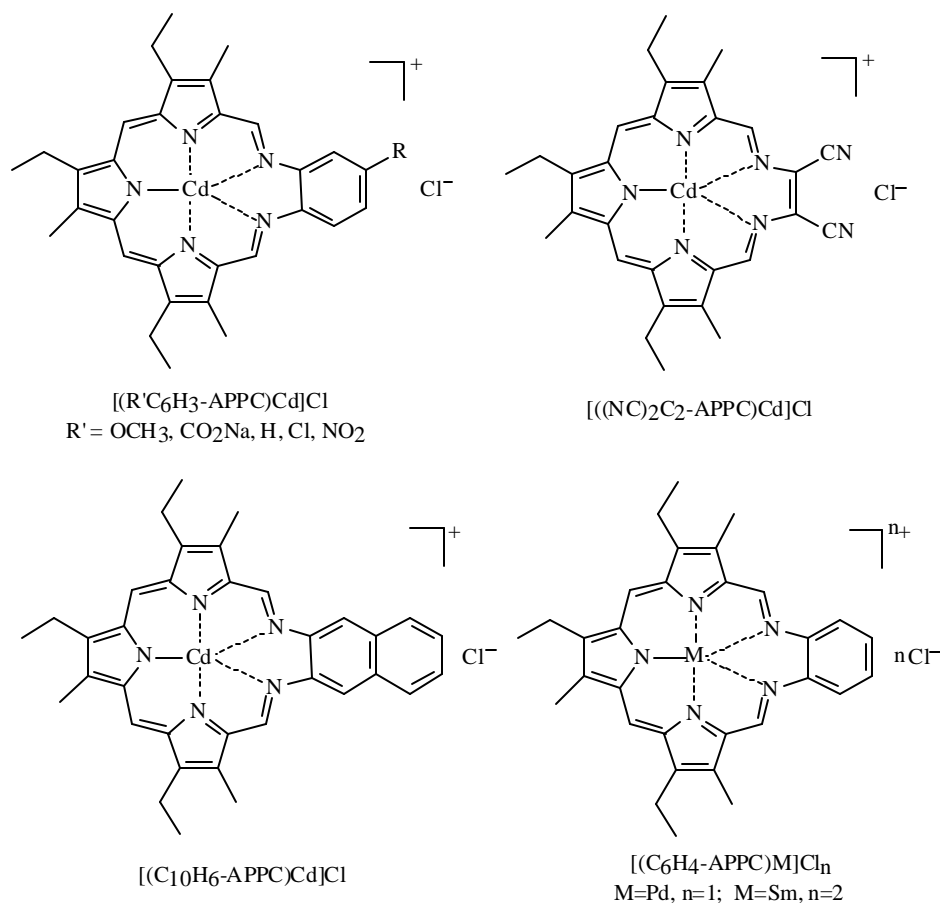


Fig. 1 Chemical structures of $[(R-APPC)M]Cl_n$ complexes

To date, the third-order nonlinear optical properties of only a few $[(R-APPC)M]Cl_n$ complexes, $[(C_6H_4-APPC)Cd]Cl$, $[(OCH_3C_6H_3-APPC)Cd]Cl$ and $[(C_6H_4-APPC)Gd]Cl_2$, have been reported.¹⁷⁻¹⁹ These studies demonstrated that the complexes have large third-order nonlinear optical susceptibilities at

both 532nm¹⁷ and 1064 nm,¹⁸ and that [(C₆H₄-APPC)Cd]Cl has a strong reverse saturable absorption (RSA) for nanosecond pulses at 532 nm.¹⁹ In addition, photolysis studies revealed that these complexes exhibit high intersystem crossing rates and high quantum yields of triplet excited states.¹⁶ These preliminary results are extremely promising, but they provide no information about the relationship between structure and nonlinear optical properties of the complexes. Recently, we have begun to study the optical limiting properties of [(R-APPC)M]Cl_n complexes (shown in Figure 1). In this paper, we summarize our results on the relationship between ligand structure and optical limiting abilities of [(R-APPC)Cd]Cl complexes²⁰ and present new results on the effect of varying the metal center in the complexes. We also compare our complexes with PbPc and SiNc, which are the strongest known absorptive optical limiting materials for nanosecond 532 nm pulses to date. As will be shown subsequently, variations in the ligand structure and metal ions have a significant effect on the optical limiting abilities of these complexes. And the optical limiting abilities of these complexes are quite comparable to that of PbPc and SiNc.

2. EXPERIMENT

The reduced macrocyclic ligands were formed by a 1:1 Schiff base condensation between a diformyltripyrane and 4-substituted-o-phenylenediamine. Subsequently, in the presence of an appropriate metal salt, the oxidation of the macrocycle as well as coordination of the metal occurred simultaneously to form the aromatic macrocyclic metal complexes. These compounds are stable at room temperature as a solid or in solution in the presence of air. Absorption spectra were acquired by using a Shimadzu UV-3101 PC UV-VIS-NIR Scanning Spectrophotometer. Samples were measured in a 2 mm quartz cell as a solution in methanol or chloroform with concentration of 3.4×10^{-4} mol/L.

The nonlinear transmission measurement was performed with a frequency-doubled Q-switched Nd:YAG laser operating at 532 nm with a temporal pulse of 5-ns (FWHM) and a repetition rate of 10 Hz. The laser pulses were focused at the center of 2 mm path-length solution cell by a 25 cm focal-length lens ($f/38$) giving an Airy spot radius of $\sim 150\mu\text{m}$. The solutions of nine different [(R-APPC)M]Cl_n complexes in methanol or chloroform were prepared at the same concentration 3.4×10^{-4} mol/L, with the internal transmittance ranging from 51% to 80%. The laser beam was divided into two beams, one was used to monitor the incident laser energy, the other was focused into the sample cell. Optical limiting is obtained by varying the input energy (E_{in}) with a half-wave plate and polarizer and by monitoring input energy (E_{in}) and output energy (E_{out}) with two J4-09 series Molelectron energy detectors. The transmitted energy was collected by a 2.54 cm focal-length lens located so as to relay the collect energy to a nominal spot size of ~ 4.0 mm on a photodiode of 0.8 cm diameter.

3. RESULTS AND DISCUSSION

To determine the viability of the series of [(R-APPC)M]Cl_n complexes as nonlinear optical materials, it is first necessary to evaluate their linear absorption. Studies of the effect of alternation of the R group and metal ion on the linear absorption of these complexes were performed, and the results are shown in Figure 2. The electronic absorption spectrum of [(C₆H₄-APPC)Cd]Cl reveals a strong Q(0,0) band absorption at 762 nm, and a ~ 80 nm red-shift with respect to the metallophthalocyanines. Hence, a relatively wide optical window is formed in the 500 ~ 660 nm region, wherein RSA may occur.

In contrast, the absorption spectra of $[(\text{NC})_2\text{C}_2\text{-APPC}]\text{Cd}]\text{Cl}$ and $[(\text{C}_{10}\text{H}_6\text{-APPC}]\text{Cd}]\text{Cl}$ show a quite different Q(0,0) band due to their different numbers of π -electrons. Most notably, $[(\text{C}_{10}\text{H}_6\text{-APPC}]\text{Cd}]\text{Cl}$, with its 26 π -electrons, exhibits a dramatically bathochromic shift combined with a more extensive window. The absorption spectra of the other four 22 π -electron $[(\text{R}'\text{C}_6\text{H}_3\text{-APPC}]\text{Cd}]\text{Cl}$ complexes are quite similar to that of $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Cd}]\text{Cl}$. Replacing H with the electron donor group, OCH_3 , induces a hyperchromic shift of the Q(0,0) band to 750 nm, while replacing H with the electron withdrawing group, NO_2 , induces a bathochromic shift of the Q(0,0) band to 792 nm. In addition, the effect of metal ions on the linear absorption is remarkable. The absorption spectrum of $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Sm}]\text{Cl}_2$ is quite similar to that of $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Cd}]\text{Cl}$, only shows approximately 10 nm bathochromic shift of Q(0,0) band and B band. However, the Q(0,0) band of $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Pd}]\text{Cl}$ obviously hyperchromic shift to 640nm (Fig. 2a), this is probably due to the different coordinating property of Pd^{2+} ion and the aggregation of solution at high concentration.

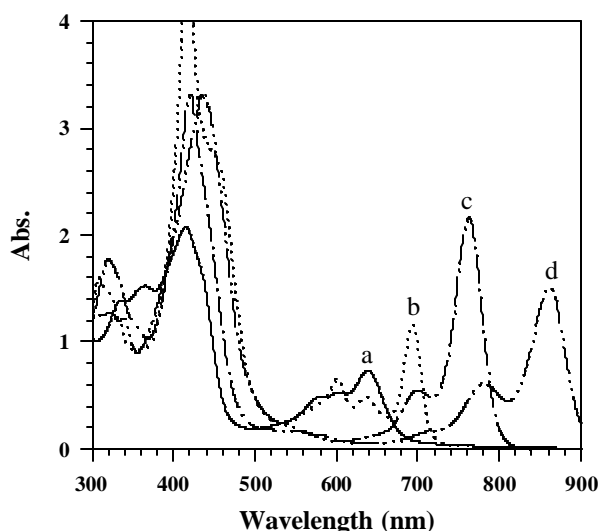


Fig. 2 Electronic absorption spectrum of (a) $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Pd}]\text{Cl}$ / chloroform, (b) $[(\text{NC})_2\text{C}_2\text{-APPC}]\text{Cd}]\text{Cl}$ / chloroform, (c) $[(\text{C}_6\text{H}_4\text{-APPC}]\text{Cd}]\text{Cl}$ / methanol and (d) $[(\text{C}_{10}\text{H}_6\text{-APPC}]\text{Cd}]\text{Cl}$ / methanol solution at 3.4×10^{-4} mol/L in 2 mm cell.

In Figure 3, the transmitted fluence of the nine complexes are shown as a function of the incident fluence. A clear RSA in the 0.01 J/cm^2 to 3.5 J/cm^2 range is exhibited by all of the complexes, with $[(\text{NC})_2\text{C}_2\text{-APPC}]\text{Cd}]\text{Cl}$ yielding results most comparable to those obtained with SiNc and PbPc (shown in Fig. 3d). This complex has an optical limiting threshold (F_{th}), defined as the incident fluence at which the center of the data band begins to deviate from the extrapolated linear transmission line,²¹ is 2.6 mJ/cm^2 . As the input fluence increases above 0.01 J/cm^2 the output-input curve bends further away from the linear transmission line until it reaches a maximum output energy where clamping occurs. The

value of the limiting throughput ($F_{through}$) is 0.31 J/cm^2 for incident fluences higher than 0.8 J/cm^2 . The transmission for this complex drops to less than 0.09 as incident fluence is increased to 3.5 J/cm^2 . The thresholds and the limiting throughputs of the other complexes and PbPc, SiNc are given in Table 1.

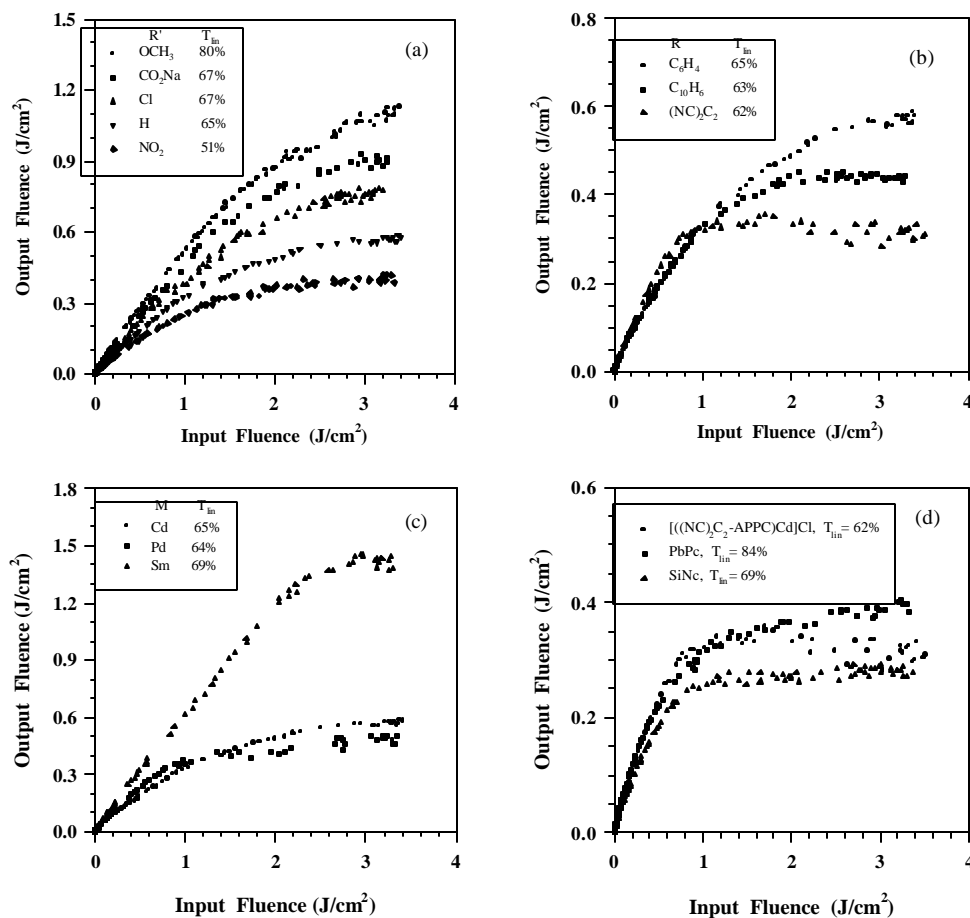


Fig. 3 Input versus output fluences of [(R-APPC)Cd]Cl complexes for 5 ns, 532 nm laser pulses at $3.4 \times 10^{-4} \text{ mol/L}$ in 2mm cell. (a) [(R'C₆H₃-APPC)Cd]Cl series, (b) [(R-APPC)Cd]Cl complexes with different numbers of π -electrons, (c) [(C₆H₄-APPC)M]Cl_h series, (d) comparison of [(NC)₂C₂-APPC)Cd]Cl with PbPc and SiNc at the same concentration of $3.4 \times 10^{-4} \text{ mol/L}$. Complexes are dissolved in methanol, except for [(NC)₂C₂-APPC)Cd]Cl, [(C₆H₄-APPC)Pd]Cl, PbPc and SiNc dissolved in chloroform.

Variations in phenylene substituents of the [(R'C₆H₃-APPC)Cd]Cl complexes have significant effects on both the linear absorption and optical limiting properties of the complexes at 532 nm. As expected, there is a roughly inverse linear relationship ($r = 0.92$) between the linear absorptions of the complexes and their limiting throughputs. However, the limiting throughputs of the complexes are also influenced by the electron donor/acceptor properties of the R group. This is exemplified by the fact that two complexes with the same linear absorption at 532 nm, [(CO₂NaC₆H₃-APPC)Cd]Cl and [(ClC₆H₃-

APPC)Cd]Cl, have quite different limiting throughputs. The limiting thresholds, F_{th} , of the [(R'C₆H₃-APPC)Cd]Cl complexes also change as the R' group is varied, but the uncertainty in these numbers precludes any discussion as to whether these changes are related to the linear absorption.

In contrast to the effects of variations of the phenylene substituents, R', variations in the conjugated bridging group, R, can independently influence the linear and nonlinear absorptions. The three compounds with different conjugated bridging groups, [(C₆H₄-APPC)Cd]Cl, [((NC)₂C₂-APPC)Cd]Cl and [(C₁₀H₆-APPC)Cd]Cl, have similar linear transmissions at 532 nm but show different optical limiting thresholds and limiting throughputs (Figure 3b). Particularly good limiting properties are exhibited by [((NC)₂C₂-APPC)Cd]Cl, and this is probably due to the strong electron-withdrawing ability of the -CN group. A similar result is seen for [(C₁₀H₆-APPC)Cd]Cl due to the effect of the conjugated naphthylene group.

Variation in the metal cation has a much large effect on the optical limiting properties than does variation of the phenylene substituents and conjugated bridging group. Figure 3c clearly demonstrates this. At similar linear transmittance, [(C₆H₄-APPC)Pd]Cl shows the lowest limiting throughput, while [(C₆H₄-APPC)Sm]Cl₂ has the highest limiting threshold and limiting throughput. The high limiting threshold and limiting throughput is connected with the lower yield of triplet excited state ($F_t \approx 0.26$) and the short lifetime of the lowest triplet excited state ($\tau_T \approx 0.55\mu\text{s}$).

In addition to the above results, we also notice that [(C₆H₄-APPC)Pd]Cl and [((NC)₂C₂-APPC)Cd]Cl, which have similar linear absorption spectra and similar linear transmittance at 532 nm, exhibit the similar optical limiting performances.

Table 1. The Linear Absorption Coefficient, the Optical Limiting Threshold and Limiting Throughput of the Nine [(R-APPC)M]Cl_n Complexes

Samples	α_0 (cm ⁻¹)	T_{lin}^c	F_{th} (mJ/cm ²)	$F_{through}$ (J/cm ²)
[(OCH ₃ C ₆ H ₃ -APPC)Cd]Cl ^a	1.12	0.28	1.5	1.13
[(CO ₂ NaC ₆ H ₃ -APPC)Cd]Cl ^a	2.00	0.26	2.5	0.90
[(C ₆ H ₄ -APPC)Cd]Cl ^a	2.15	0.16	1.8	0.56
[(ClC ₆ H ₃ -APPC)Cd]Cl ^a	2.00	0.24	1.8	0.77
[(NO ₂ C ₆ H ₃ -APPC)Cd]Cl ^a	3.37	0.10	1.4	0.40
[(C ₆ H ₄ -APPC)Pd]Cl ^b	2.23	0.14	3.0	0.48
[(C ₆ H ₄ -APPC)Sm]Cl ₂ ^a	1.93	0.42	150.0	1.42
[((NC) ₂ C ₂ -APPC)Cd]Cl ^b	2.39	0.09	2.6	0.31
[(C ₁₀ H ₆ -APPC)Cd]Cl ^a	2.31	0.13	3.0	0.44
PbPc ^b	0.87	0.11	4.0	0.39
SiNc ^b	1.86	0.09	3.5	0.28

a. In methanol.

b. In chloroform.

c. The limiting transmittance at 3.5J/cm².

A figure of merit for RSA molecules involving an excited triplet state can be defined as $s_t / s_g \approx \ln T_{sat} / \ln T_{lin}$,⁸ where T_{sat} is the value of the transmission for which the slope of the transmission versus input fluence line approximates zero. The conditions for this figure of merit are that the pulsewidth is longer than the intersystem crossing time, the incident fluence exceeds the saturable fluence $F_{sat} = h\nu / s_g F_t$, and the quantum yield of triplet excited state is quite high. These conditions are met by the [(R-APPC)M]Cl_n complexes. These complexes exhibit F_{sat} values that range from 0.04 J/cm² to 0.12 J/cm², implying that for fluences between 0.3~3.5 J/cm², the ground state will be greatly bleached. Further, the small intersystem crossing time and the high quantum yields of the triplet excited states¹⁶ for these molecules indicate that the excited state is distributed mainly to the lowest triplet excited state over the duration of one laser pulse.

In our current experimental setup, the damage threshold for the optical cell limits the maximum fluence, and we are unable to reach saturable transmission for the complexes. Hence we can only calculate lowest bounds for the s_t / s_g values of the [(R-APPC)M]Cl_n complexes (Table 2). Nevertheless, these s_t / s_g values are extremely promising because they closely approach those obtained with SiNc and PbPc, 32 and 23, respectively.¹⁰ The great ease of structural modification of our complexes may allow for values of s_t / s_g that surpass those of the complexes measured in this paper. Moreover, the complexes in this paper already exhibit higher quantum yields of triplet excited states than does SiNc, as well as F_{th} and $F_{through}$ values that are comparable to those of SiNc and PbPc.

Table 2. The Photophysical Properties and the Ratio of Lowest Triplet Excited-state to Ground-state Absorption Cross-section (s_t / s_g) for Nine [(R-APPC)M]Cl_n Complexes

Samples	F_t	F_{sat} (J/cm ²)	s_g (10 ⁻¹⁷ cm ²)	s_t / s_g
[(OCH ₃ C ₆ H ₃ -APPC)Cd]Cl ^a	0.89 ^c	0.076	0.55	>5.7
[(CO ₂ NaC ₆ H ₃ -APPC)Cd]Cl ^a	0.47 ^c	0.080	0.99	>3.4
[(C ₆ H ₄ -APPC)Cd]Cl ^a	0.91 ^c	0.037	1.10	>4.3
[(ClC ₆ H ₃ -APPC)Cd]Cl ^a	0.78 ^c	0.048	0.99	>3.6
[(NO ₂ C ₆ H ₃ -APPC)Cd]Cl ^a	0.60 ^c	0.038	1.62	>3.4
[(C ₆ H ₄ -APPC)Pd]Cl ^b	—	—	1.14	>4.3
[(C ₆ H ₄ -APPC)Sm]Cl ₂ ^a	0.26 ^c	0.122	0.95	>2.3
[(NC) ₂ C ₂ -APPC]Cd]Cl ^b	—	—	1.18	>5.0
[(C ₁₀ H ₆ -APPC)Cd]Cl ^b	0.32 ^c	0.102	1.14	>4.4
PbPc ^b	0.92 ^d	0.091	0.43	>12.7
SiNc ^b	0.23 ^e	0.177	0.92	>6.5

a. In methanol. b. In chloroform. c. Ref. 16 d. Ref. 8 e. Ref. 22

4. CONCLUSION

The induced absorption from the [(R-APPC)M]Cl_n complexes is sufficiently fast to provide optical limiting on a nanosecond time scale. The optical limiting performance of these complexes is

comparable to that of the most promising complexes in the literature. Moreover, these preliminary studies suggest that it will be possible to optimize the optical limiting properties of the complexes by varying the conjugated bridging R group and metal ion. With further development, these complexes may ultimately prove to be an important new class of materials for optical power limiters.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1. *Organic Materials for Nonlinear Optics*, edited by R. A. Hann and D. Bloor (The Royal Society of Chemistry, 1989).
2. *Organic Molecules for Nonlinear Optics and Photonics*, edited by J. Messier, F. Kajzar, and P. Prasad, *NATO ASI Ser. E* **194** (Kluwer, Dordrecht, 1991).
3. T. J. Bunning, L. V. Natarajan, M. G. Schmitt, B. L. Epling, and R. L. Crane, "Optical limiting in solutions of diphenyl polyenes", *Appl. Opt.* **30** (30), 4341 (1991).
4. Rama Chari, S. R. Mishra, H. S. Rawat, and S. M. Oka, "Reverse saturable absorption and optical limiting in indanthrone dyes", *Appl. Phys. B* **62**, 293 (1996).
5. D. R. Coulter, V. M. Miskowski, J. W. Perry, T-H. Wei, E. W. Van Stryland, and D. J. Hagan, "Optical limiting in solution of metallo-phthalocyanines and naphthalocyanines", *Proc. SPIE* **1105**, 42 (1989).
6. J. W. Perry, L. R. Khundkar, D. R. Coulter, D. Alvarez, Jr., S. R. Marder, T-H. Wei, M. J. Sence, E. W. Van Stryland, and D. J. Hagan, "Excited state absorption and optical limiting in solutions of metallophthalocyanines", in *Organic Molecules for Nonlinear Optics and Photonics*, edited by J. Messier, F. Kajzar, P. Prasad, *NATO ASI Ser. E* **194**, 369 (Kluwer, Dordrecht, 1991).
7. T. H. Wei, D. J. Hagan, M. J. Sence, E. W. Van Stryland, J. W. Perry, and D. R. Coulter, "Direct measurements of nonlinear absorption and refraction in solutions of phthalocyanines", *Appl. Phys. B* **54**, 46 (1992).
8. J. W. Perry, K. Mansour, S. R. Marder, K. J. Perry, D. Alvarez, Jr., and I. Choong, "Enhanced reverse saturable absorption and optical limiting in heavy-atom-substituted phthalocyanines", *Opt. Lett.* **19**(9), 625 (1994).
9. J. S. Shirk, R. G. Pong, F. J. Bartoli, and A. W. Snow, "Optical limiter using a lead phthalocyanine", *Appl. Phys. Lett.* **63** (14), 1880 (1993).
10. K. Mansour, D. Alvarez, Jr., K. J. Perry, I. Choong, S. R. Marden, and J. W. Perry, "Dynamics of optical limiting in heavy-atom substituted phthalocyanines", *Proc. SPIE* **1853**, 132 (1993).
11. W. Blau, H. Byrne, W. M. Dennis, and J. M. Kelly, "Reverse saturable absorption in tetraphenylporphyrins", *Opt. Commun.* **56**, 25 (1985).
12. G. L. Wood, M. J. Miller, and A. G. Mott, "Investigation of tetrabenzporphyrin by the Z-scan technique", *Opt. Lett.* **20** (9), 973 (1995).
13. L. W. Tutt and A. Kost, "Optical limiting performance of C₆₀ and C₇₀ solutions", *Nature* **356**, 225 (1992).
14. J. Staromlynska, P. B. Chapple, J. R. Davy, and T. J. McKay, "A platinum ethynyl compound for optical limiting", *Proc. SPIE* **2229**, 59 (1994).
15. W. Sun and D. Wang, "The synthesis and characterization of asymmetric pentaazadentate porphyrin-like metal complexes", *Chin. Chem. Lett.* **4** (3), 225 (1993).
16. W. Sun and D. Wang, "Excited-state properties of asymmetric pentaazadentate expanded porphyrins", *Science in China (Series B)* **39** (5), 509 (1996).
17. J. Si, Y. Wang, J. Zhao, P. Ye, D. Wang, W. Sun, and S. Dong, "Fluence dependence of nonlinear optical response of cadmium texaphyrin", *Appl. Phys. Lett.* **67**(14), 1975 (1995).

18. Q. Gong, Y. Wang, S. Yang, Z. Xia, Y. H. Zou, W. Sun, S. Dong, and D. Wang, "Third-order optical nonlinearities of new two-dimensional π -conjugated metal-coordinated complexes", *J. Phys. D: Appl. Phys.* **27**, 911 (1994).
19. J. Si, M. Yang, Y. Wang, L. Zhang, C. Li, D. Wang, S. Dong, and W. Sun, "Nonlinear excited state absorption in cadmium texaphyrin solution", *Appl. Phys. Lett.* **64** (23), 3083 (1994).
20. W. Sun, C. C. Byeon, M. M. McKerns, C. M. Lawson, G. M. Gray, D. Wang, "Optical limiting performances of asymmetric pentaazadentate porphyrin-like cadmium complexes", accepted by *Appl. Phys. Lett.* (1998).
21. A. Hochbaum, Y. Y. Hsu, and J. L. Fergason, "Molecular structure and its relation to optical limiting", *Proc. SPIE* **2229**, 48 (1994).
22. P. A. Firey, W. E. Ford, J. R. Sounik, M. E. Kenney, and M. A. Rodgers, "Silicon naphthalocyanine triplet state and oxygen: a reversible energy-transfer reaction", *J. Am. Chem. Soc.* **110**, 7626 (1988).