

Optical limiting performances of asymmetric pentaazadentate porphyrin-like cadmium complexes

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The optical limiting performances of seven asymmetric pentaazadentate porphyrin-like cadmium complexes 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 ~ 3.0 mJ/cm². The throughputs of these complexes were limited to 0.31 ~ 1.13 J/cm² for incident fluences as high as 3.5 J/cm². The limiting throughput was strongly influenced by the nature of the ligand. Lower bounds for the ratio of triplet excited-state to ground-state absorption cross sections have been estimated at 3.4 ~ 5.7. The lower limiting thresholds, lower limiting throughputs, as well as the ease of modification of the ligands, make these complexes promising candidates for optical power limiters.

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The need for passive optical limiters to protect human eyes and sensors from intense optical beams has generated much interest in the development of optical limiting materials.¹⁻⁹ Metallophthalocyanines and metallonaphthalocyanines⁶⁻⁹ are among the most promising molecular materials for use in these devices 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, 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 is the asymmetric pentaazadentate porphyrin-like metal complexes $[(R-APPC)M]Cl_n$,^{10,11} 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. Such structural modifications should allow $[(R-APPC)M]Cl_n$ complexes with optimal photophysical properties for a variety of applications to be developed.

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.¹²⁻¹⁴ These studies demonstrated that the complexes have large third-order nonlinear optical susceptibilities at both 532nm¹² and 1064 nm,¹³ and that $[(C_6H_4-APPC)Cd]Cl$ has a strong reverse saturable absorption (RSA) for nanosecond pulses at 532 nm.¹⁴ In addition, photolysis studies revealed that these complexes exhibit high intersystem crossing rates and high quantum yields of triplet excited states.¹¹ These

preliminary results are extremely promising, but they provide no information about the relationship between ligand structure and nonlinear optical properties of the complexes. In this paper, we report the first study of the relationship between ligand structure and optical limiting abilities of [(R-APPC)Cd]Cl complexes (shown in Figure 1). As will be shown subsequently, variations in the ligand structure have a significant effect on the optical limiting abilities of these complexes.

To determine the viability of the series of [(R-APPC)Cd]Cl complexes as nonlinear optical materials, it is first necessary to evaluate their linear absorption. Studies of the effect of alternation of the R group 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 [((NC)₂C₂-APPC)Cd]Cl and [(C₁₀H₆-APPC)Cd]Cl show a quite different Q(0,0) band due to their different numbers of π -electrons. Most notably, [(C₁₀H₆-APPC)Cd]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 [(R'C₆H₃-APPC)Cd]Cl complexes are quite similar to that of [(C₆H₄-APPC)Cd]Cl. Replacing H with the electron donor group, OCH₃, induces a hyperchromic shift of the Q(0,0) band to 750 nm, while replacing H with the electron withdrawing group, NO₂, induces a bathochromic shift of the Q(0,0) band to 792 nm.

Nonlinear transmission measurements of the seven [(R-APPC)Cd]Cl complexes were conducted, using a standard experimental configuration.¹⁵ A frequency-doubled (532

nm), Q-switched Nd:YAG laser with 5 ns pulses and a repetition rate of 10 Hz was used to excite the sample. The laser pulses were focused at the center of a 2 mm path-length cell by a 25 cm focal-length lens ($f/38$) giving an Airy spot radius of $\sim 150\mu\text{m}$. Input and output energies were measured by two J4-09 series Molelectron energy detectors. The concentration was 3.4×10^{-4} mol/L for all complexes and the internal transmittance ranged from 51% to 80%. In Figure 3, the transmitted fluence of the seven 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^4 and $\text{PbPc}^{4,5}$. This complex has an optical limiting threshold¹⁶ (F_{th}) of 2.6 mJ/cm^2 , and 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 are given in Table I.

Variations in phenylene substituents of the $[(\text{R}'\text{C}_6\text{H}_3\text{-APPC})\text{Cd}]\text{Cl}$ 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, $[(\text{CO}_2\text{NaC}_6\text{H}_3\text{-APPC})\text{Cd}]\text{Cl}$ and $[(\text{ClC}_6\text{H}_3\text{-APPC})\text{Cd}]\text{Cl}$, have quite different limiting throughputs. The limiting thresholds, F_{th} , of the $[(\text{R}'\text{C}_6\text{H}_3\text{-APPC})\text{Cd}]\text{Cl}$ 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.

A figure of merit for RSA molecules involving an excited triplet state can be defined as $S_t/S_g \approx \ln T_{sat}/\ln T_{lin}$,⁴ 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)Cd]Cl 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 time¹² and the high quantum yields of the triplet excited states¹¹ 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)Cd]Cl complexes (Table I). Nevertheless, these s_t/s_g values are extremely promising because they closely approach those obtained with SiNc and PbPc, 32 and 23, respectively.⁶ 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 SiNc⁴ and PbPc.^{4,5}

In summary, the induced absorption from the [(R-APPC)Cd]Cl 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. With further development, these complexes may ultimately prove to be an important new class of materials for optical power limiters.

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TABLE I. The photophysical properties and optical limiting properties of seven [(R-APPC)Cd]Cl complexes (solution concentrations: 3.4×10^{-4} mol/L)

Samples	α_0	T_{lim}^c	F_t^d	F_{th}	$F_{through}$	s_t/s_g
	(cm^{-1})			(mJ/cm^2)	(J/cm^2)	
[(OCH ₃ C ₆ H ₃ -APPC)Cd]Cl ^a	1.12	0.28	0.89	1.5	1.13	>5.7
[(CO ₂ NaC ₆ H ₃ -APPC)Cd]Cl ^a	2.00	0.26	0.47	2.5	0.90	>3.4
[(C ₆ H ₄ -APPC)Cd]Cl ^a	2.15	0.16	0.91	1.8	0.56	>4.3
[(ClC ₆ H ₃ -APPC)Cd]Cl ^a	2.00	0.24	0.78	1.8	0.77	>3.6
[(NO ₂ C ₆ H ₃ -APPC)Cd]Cl ^a	3.37	0.10	0.60	1.4	0.40	>3.4
[(NC) ₂ C ₂ -APPC)Cd]Cl ^b	2.39	0.09	—	2.6	0.31	>5.0
[(C ₁₀ H ₆ -APPC)Cd]Cl ^a	2.31	0.13	0.32	3.0	0.44	>4.4

a. In methanol.

b. In chloroform.

c. The limiting transmittance at $3.5 \text{ J}/\text{cm}^2$.

d. Ref. 11.

Captions of figures

FIG. 1 Chemical structures of [(R-APPC)Cd]Cl complexes.

FIG. 2 Electronic absorption spectrum of [(C₆H₄-APPC)Cd]Cl, [(C₁₀H₆-APPC)Cd]Cl in methanol, and [((NC)₂C₂-APPC)Cd]Cl in chloroform solution at 3.4×10^{-4} mol/L in 2 mm cell.

FIG. 3 Input versus output fluences of [(R-APPC)Cd]Cl complexes for 5 ns, 532 nm laser pulses at 3.4×10^{-4} mol/L in 2mm cell. (a) [(R'C₆H₃-APPC)Cd]Cl series, (b) [(R-APPC)Cd]Cl complexes with different numbers of π -electrons. Complexes are dissolved in methanol, except for [((NC)₂C₂-APPC)Cd]Cl dissolved in chloroform.

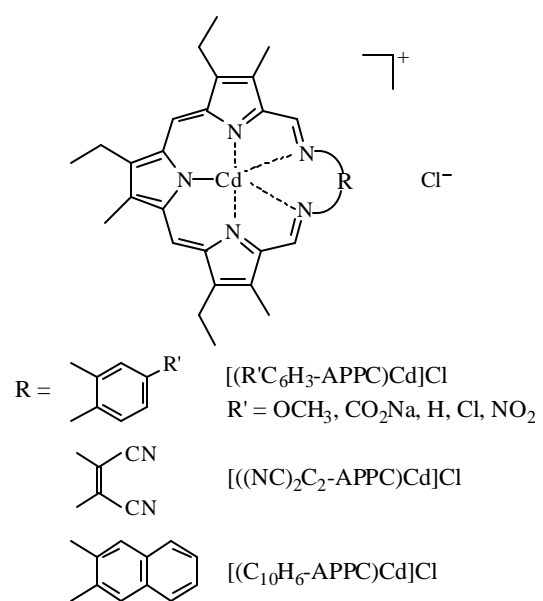


FIG. 1 L-5269 (Wenfang Sun, *et al.*)

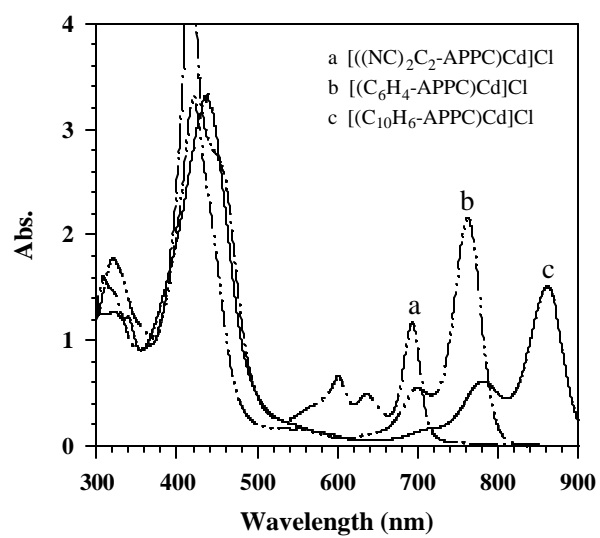


FIG. 2 L-5269 (Wenfang Sun, *et al.*)

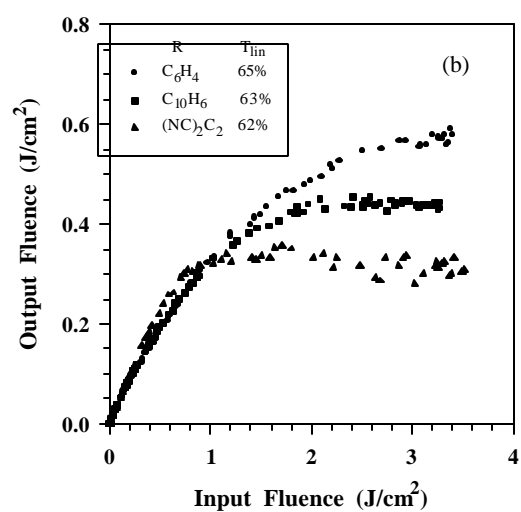
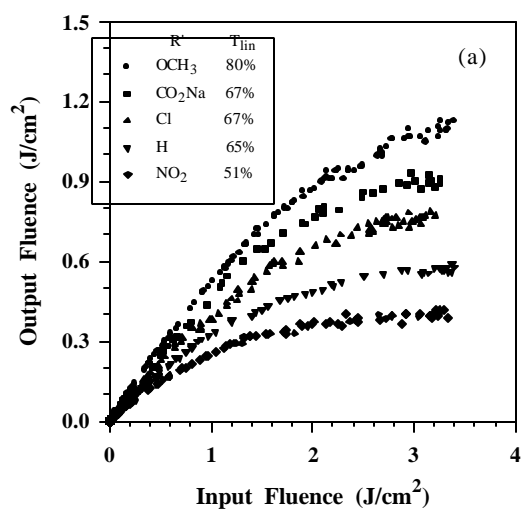


FIG. 3 L-5269 (Wenfang Sun, *et al.*)