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Microwave-assisted synthesis and reverse saturable absorption of phthalocyanines and porphyrins

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Abstract

Soluble phthalocyanines, including tetrakis(2,9,16,23-cumylphenoxy) copper phthalocyanines ($CuPc(\beta\text{-}CP)_4$), tetrakis(1,8,15,22-cumylphenoxy) copper phthalocyanines ($CuPc(\alpha\text{-}CP)_4$) as well as tetrakis(2,9,16,23-*tert*-butyl) copper phthalocyanines ($CuPc(\beta\text{-}t\text{-}butyl)_4$), and porphyrins (5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrins; M(TBP), M = H_2, Zn, Cu, Mg, InCl, AlCl) have been quickly synthesized by microwave irradiation. Furthermore, their reverse saturable absorption have also been investigated by dissolving them in solvent or incorporating them in polymer-silica hybrid material with a sol–gel process with polyvinyl butyral and tetraethyl orthosilicate as precursors. A new method for the preparation process of phthalocyanines and porphyrins in the solids has been successfully used.
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1. Introduction

Phthalocyanines and porphyrins have attracted attention for many decades because of their comprehensive applications such as molecular thermometers [1], light-emitting diodes [2,3], magnets [4], solar cells [5,6], and photodynamic therapy [7]. In recent years, porphyrin and phthalocyanines molecules have been observed to exhibit reverse saturable absorption (RSA) [8,9] in solutions due to their planar π-conjugated electron systems. Materials with strong RSA can effectively limit the output energy of incident light. Such materials are of prime importance in optical limiting applications [10,11]. However, the RSA of phthalocyanines and porphyrins in the thin solid film are less studied. Furthermore, the conventional syntheses for both of these two materials are time-consuming [12–15].

In this paper, we have rapidly prepared phthalocyanines as well as porphyrins by microwave irradiation and incorporated them in polymer-silica hybrid material with a sol–gel process with polyvinyl butyral (PVB) and tetraethyl orthosilicate (TEOS) as precursors to form organic–inorganic hybrids, which have the advantages of excellent flexibility, high glass transition temperature, good transparency, and feasibility as device substrates, for the industrial practicability. By utilizing *Z*-scan technique with picosecond (ps) laser pulses at 532 nm, the RSA of phthalocyanines and porphyrins in solvent and sol–gel TEOS/PVB hybrid film have been quantitatively characterized.

2. Experimental

2.1. Preparation of dyes and organic–inorganic hybrid films

2.1.1. Preparation of tetrakis(2,9,16,23-cumylphenoxy) copper phthalocyanines (CuPc(β-CP)₄) (Scheme 1) and tetrakis(1,8,15,22-cumylphenoxy) copper phthalocyanines (CuPc(α-CP)₄) (Scheme 2)

4-Nitrophthalonitrile (2 g, 11.55 mmol), 4-cumylphenol (2.45 g, 11.55 mmol), potassium carbonate (2.5 g,

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18.1 mmol) and N,N-dimethylformamide (DMF) (15 ml) were irradiated in a quartz vessel of 50 ml by a microwave oven at 440 W for 10 min. After washed with a methanol/water solution (v/v = 1/1) and purified by recystallization with methanol, 4-cumylphenoxy-4-phthalonitrile (3.06 g) was obtained (yield: 78%). IR (KBr) (cm^{-1}) (4-cumylphenoxy-4-phthalonitrile): 3050, 2914, 2250, 1601, 1511, 1300, 1242, 1184, 1096, 1010, 910, 821, 786, 711, 592, 575.

4-Cumylphenoxy-4-phthalonitrile (1 g, 2.96 mmol) and copper chloride (0.2 g, 1.49 mmol) in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (5 ml) were irradiated in a quartz vessel of 50 ml by a microwave oven at 440 W for 10 min. The product was washed with a methanol/water solution (v/v, 1/2) and purified by column chromatography (silica gel, tetrahydrofuran/ ethyl acetate/methanol = 4/1/1, wt/wt/wt). After drying, CuPc(β-CP)$_4$ (0.81 g) was obtained (yield: 77%). IR (KBr) (cm^{-1}) (CuPc(β-CP)$_4$): 3047, 2952, 1615, 1604, 1512, 1445, 1344, 1317, 1251, 1221, 1190, 1132, 1085, 1043, 912, 817, 740, 661, 622 cm^{-1}. UV [toluene, λ_{max}] 680, 612, 349 nm. MS: m/z 1417 (FAB$^+$). Elemental analysis for C$_{92}$H$_{72}$N$_8$O$_4$Cu, Calc. C, 77.97; H, 5.12 ; N, 7.91. Found: C, 77.83; H, 5.19; N, 7.57%.

The same procedure was adopted in the preparation of CuPc(α-CP)$_4$ except that the starting material was 3-nitrophthalonitrile. The yield was 71%. IR (KBr) (cm^{-1}) (CuPc(α-CP)$_4$): 3045, 2951, 1613, 1602, 1515, 1441, 1341, 1315, 1253, 1219, 1192, 1131, 1081, 1042, 915, 813, 742, 657, 618 cm^{-1}. UV [toluene, λ_{max}] 695, 625, 334 nm. MS: m/z 1417 (FAB$^+$). Elemental analysis for C$_{92}$H$_{72}$N$_8$O$_4$Cu, Calc. C, 77.97; H, 5.12 ; N, 7.91. Found: C, 77.69; H, 5.20; N, 7.20%.

2.1.2. Preparation of tetrakis(2,9,16,23-tert-butyl) copper phthalocyanines (CuPc(β-t-butyl)$_4$) (Scheme 3)

4-tetra-t-Butyl phthalonitrile (1 g, 5.44 mmol) and copper chloride (0.37 g, 2.72 mmol) in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (5 ml) were irradiated in a quartz vessel of 50 ml by a microwave oven at 440 W for 10 min. The product was washed with a methanol/water solution (v/v, 1/2) and purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/4, wt/wt). After drying, CuPc(β-t-butyl)$_4$ (0.81 g) was obtained (yield: 74%). IR (KBr)(CuPc(β-t-butyl)$_4$): 2953, 1611, 1609, 1448, 1359, 1317, 1253, 1221, 1195, 1140, 1088, 1046, 914, 822, 742, 665, 532, 503 cm^{-1}. UV [toluene, λ_{max}] 677, 610, 346 nm. MS: m/z 800 (FAB$^+$). Elemental analysis for C$_{48}$H$_{48}$N$_8$Cu:, Calc. C, 72.02; H, 6.04 ; N, 14.00. Found: C, 72.31; H, 6.27; N, 13.80%.

2.1.3. Preparation of 5,10,15,20-tetrakis(4-tert-butylphenyl)porphyrins ((M(TBP), M = H$_2$, Mg, Zn, Cu, InCl, AlCl) (Scheme 4)

4-tertbutyl benzaldehyde (3 g, 18.5 mmol), pyrrole (1.34 g, 20 mmol), and propionic acid (10 ml) were ir-

radiated in a quartz vessel of 50 ml by a microwave oven at 560 W for 5 min. The crude product was washed with distilled water and purified by recystallization with toluene. After purified by column chromatography (aluminum oxide, chloroform), H$_2$(TBP) (2.18 g) was obtained (yield: 56%).

IR (KBr) (cm^{-1}) (H$_2$(TBP)): 3416, 2959, 2853, 1664, 1646, 1601, 1568, 1550, 1531, 1502, 1465, 1410, 1391, 1362, 1329, 1295, 1266, 1196, 1155, 1141, 1107, 1089, 1019, 960, 879, 838, 764, 709, 665, 558, 425. UV–Vis λ_{max} (nm) 545, 513, 415 (in ethanol). MS: (m/z) (FAB$^+$) 840. Elemental analysis for C$_{60}$H$_{62}$N$_4$, Calc. C, 85.88; H, 7.45 ; N, 6.68. Found: C, 85.72; H, 7.33; N, 6.52%.

H$_2$(TBP) (1 g, 1.2 mmol) and magnesium chloride (0.17 g, 1.79 mmol) were ground together in a quartz vessel of 50 ml, poured into 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 5 ml) as catalyst, and irradiated in a microwave oven at 240 W for 5 min. The crude product was firstly dissolved in ethanol, and then butyl acetate as well as petroleum ether was added for precipitation. After purified by recystallization with methanol and by column chromatography (aluminum oxide, chloroform), Mg(TBP)(0.75 g) was obtained (yield = 72%).

IR (KBr) (cm^{-1}) (Mg(TBP)): 2941, 2857, 1664, 1644, 1611, 1552, 1535, 1513, 1482, 1465, 1443, 1387, 1359, 1320, 1267, 1233, 1200, 1107, 1020, 990, 956, 914, 883, 836, 794, 716, 665, 647, 536, 514, 464, 441. UV–Vis λ_{max} (nm) 610, 565, 431 (in 1-methyl-2-pyrrolidone (NMP)). MS: (m/z) (FAB$^+$) 861. Elemental analysis for C$_{60}$H$_{60}$N$_4$Mg, Calc. C, 83.65; H, 7.02 ; N, 6.50. Found: C, 85.55; H, 7.13; N, 6.35%.

The same procedure was adopted in the preparation of Zn(TBP), Cu(TBP), InCl(TBP), and AlCl(TBP). The yields of Zn(TBP), Cu(TBP), InCl(TBP), and AlCl(TBP) were 65%, 77%, 71%, 68%, respectively.

IR (KBr) (cm^{-1}) (Zn(TBP)): 2952, 1719, 1636, 1561, 1462, 1269, 1191, 1096, 1011, 972, 845, 799, 741, 559. UV–Vis λ_{max} (nm) 612, 551, 425 (in NMP). MS: (m/z) (FAB$^+$) 902. Elemental analysis for C$_{60}$H$_{60}$N$_4$Zn, Calc. C, 79.85; H, 6.70; N, 6.21. Found: C, 79.72; H, 6.81; N, 6.13%.

IR (KBr) (cm^{-1}) (Cu(TBP)): 2947, 1715, 1632, 1558, 1467, 1267, 1188, 1092, 1016, 975, 848, 802, 745, 554. UV–Vis λ_{max} (nm) 609, 543, 419 (in NMP). MS: (m/z) (FAB$^+$) 900. Elemental analysis for C$_{60}$H$_{60}$N$_4$Cu, Calc. C, 80.01; H, 6.71; N, 6.22. Found: C, 79.88; H, 6.65; N, 6.11%.

IR (KBr) (cm^{-1}) (InCl(TBP)): 2950, 1716, 1631, 1557, 1458, 1261, 1184, 1096, 1018, 971, 850, 805, 747, 551. UV–Vis λ_{max} (nm) 615, 561, 428 (in NMP). MS: (m/z) (FAB$^+$) 951. Elemental analysis for C$_{60}$H$_{60}$N$_4$InCl, Calc. C, 72.98; H, 6.12; N, 5.67. Found: C, 72.85; H, 6.03; N, 5.72%.

IR (KBr) (cm^{-1}) (AlCl(TBP)): 2955, 1711, 1628, 1563, 1455, 1253, 1177, 1092, 1011, 965, 853, 801, 752, 555. UV–Vis λ_{max} (nm) 618, 564, 430 (in NMP). MS: (m/z) (FAB$^+$) 899. Elemental analysis for C$_{60}$H$_{60}$N$_4$AlCl, Calc. C, 80.11; H, 6.72; N, 6.23. Found: C, 80.22; H, 6.66; N, 6.26%.

2.1.4. Preparation of dye/TEOS/PVB hybrid films

Sol A was prepared by mixing TEOS, H_2O, ethanol, and 1N $HCl_{(aq.)}$ (1:8:3:10^{-4} = mole ratio) together. The mixture was stirred at room temperature for 12 h to obtain a homogeneous solution. Sol B was prepared by dissolving dye (phthalocyanine or porphyrin) and polyvinyl butyral (PVB) in propylene glycol methyl ether acetate. Then Sol A and Sol B were mixed and stirred at 60 °C for 12 h. By casting the gel, the hybrid films were made. The films were dried slowly in air at room temperature for one day, then the gels were vacuum-dried at 50 °C for 3 h and 130 °C for 2 h, respectively. Finally, transparent dried films were obtained. The concentrations of dye in the TEOS/PVB matrix were 15 wt%. The thickness of the films were ≈100 μm.

2.2. Z-scan measurements

The Z-scan experiments were executed on the hybrid films and toluene or NMP solutions of phthalocyanines and porphyrins. This technique has been introduced previously [16]. In this study, a Q-switched and mode-locked Nd:YAG laser operated in the TEM_{00} mode at 10 Hz was used. The laser is frequency-doubled to give an output wavelength ($\lambda = 532$ nm) and tightly focused

to have a radius of $\omega_0 = 28$ μm at e^{-2} of maximum intensity at the focus. The pulse has a half-width of $\tau = 16.3$ ps at e^{-1} of maximum intensity (HW $e^{-1}M$).

The films doped with porphyrins or phthalocyanines were put on the side of quartz vessel, and the laser can penetrate through them. All the solution samples were prepared to have a concentration of 10^{-4} M and contained in a 1 mm quartz cell.

3. Results and discussion

3.1. Microwave-assisted process

Microwave-assisted process has recently been a fast tool for chemical synthesis [17]. In this paper, the procedure for preparation of phthalocyanines and porphyrins, including dehydrobromonation, tetracyclomerization, dehydration, and replacement of protons to metal ions as shown in Schemes 1–4, take only 5–10 min. However, the conventional methods take several hours to one day for completion [12–15]. Microwave irradiation accelerates the polarization of the starting materials to promote the reactions. In comparison with previous other papers about microwave-assisted preparation of phthalocya-
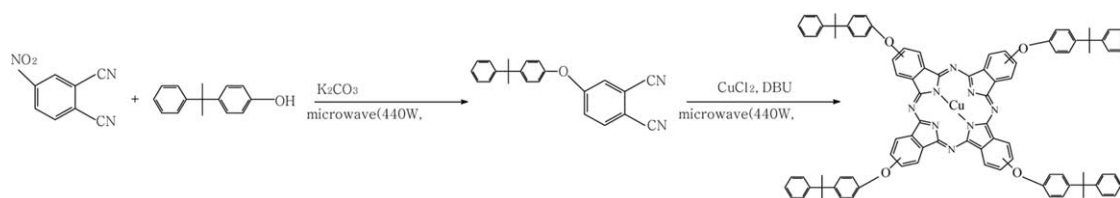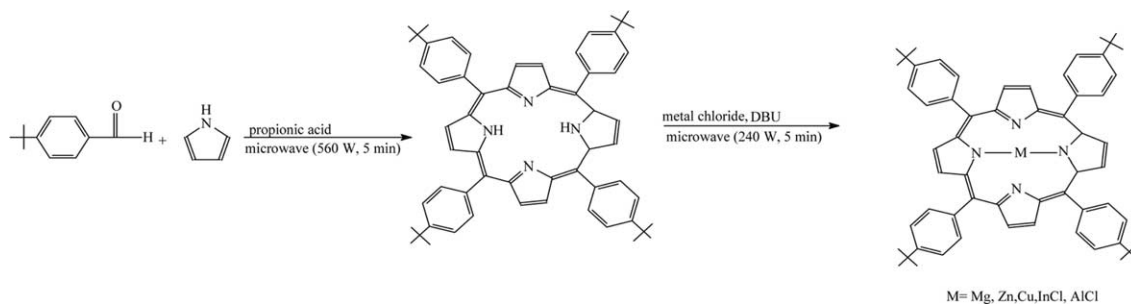
Scheme 1.
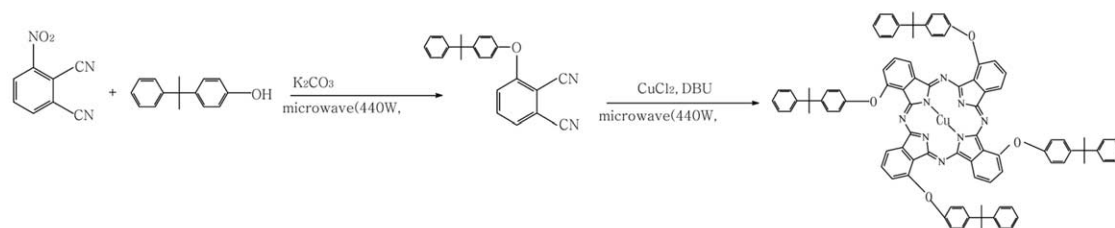
Scheme 2.
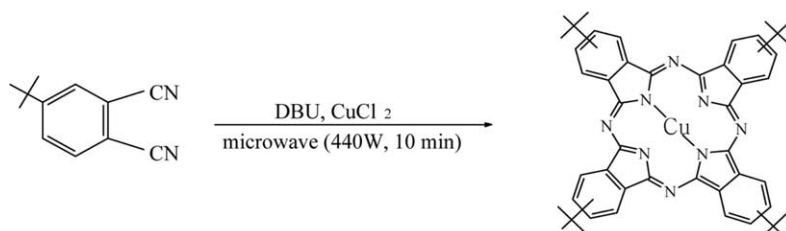
Scheme 3.

Scheme 4.

nines and porphyrin [18–21], no solvent is necessary in the reactions described in this paper and the reaction condition is mild. These advantages are paramount to fit the demand in the clean and low-cost production of soluble porphyrins and phthalocyanines. The reactions mentioned in this paper have also been successfully repeated several times with identical results.

3.2. Thermal properties

Thermal characterization of TEOS/PVB hybrid film doped with CuPc(β-t-butyl)$_4$ and Zn(TBP) were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA) instrument and shown in Fig. 1. Their decomposition temperatures (at 5% weight loss) are higher than 350 °C. This shows TEOS/PVB hybrid films doped with phthalocyanines and porphyrins have excellent thermal stability and can refrain from thermal decomposition when the laser penetrates through them.

3.3. RSA properties

3.3.1. RSA properties of phthalocyanines

Because of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, phthalocyanines usually exhibit two characteristic absorptions [22], which are B band (300–400 nm) and Q band (600–800 nm), respectively. For phthalocyanine molecules, the interesting region of optical limiting effect lies in the highly transparent regime between 450 and 550 nm. We focused the region near 532 nm for instrumental consideration. As shown in Fig. 2, the absorption spectra of CuPc(α-CP)$_4$, CuPc(β-CP)$_4$, and CuPc(β-t-butyl)$_4$ in toluene and those in hybrid film are quite different due to aggregation taken place in hybrid film. Aggregation results from the result of strong intermolecular interaction between the dyes and the matrix, which leads to blue shift and the broadness of band shape.

We numerically fit the Z-scan results, as shown in Figs. 3 and 4, by the method reported previously [23]. The best fits are obtained with the appropriate values of σ_{S1} (absorption cross section of excited state) shown in Table 1. The absorption cross section of ground state (σ_{S0}) is obtained by Eqs. (1)–(4) while α was measured in the linear region of the Z-scan apparatus.

$$\frac{\mathrm{d}I}{\mathrm{d}z'} = -\alpha I, \tag{1}$$

where z' is the penetration of the light into the sample.

$$T \equiv \frac{I_l}{I_0} = \mathrm{e}^{-\alpha l}, \tag{2}$$

where I_l represents the intensity at the rear surface of the sample and l denotes the sample thickness of sample.
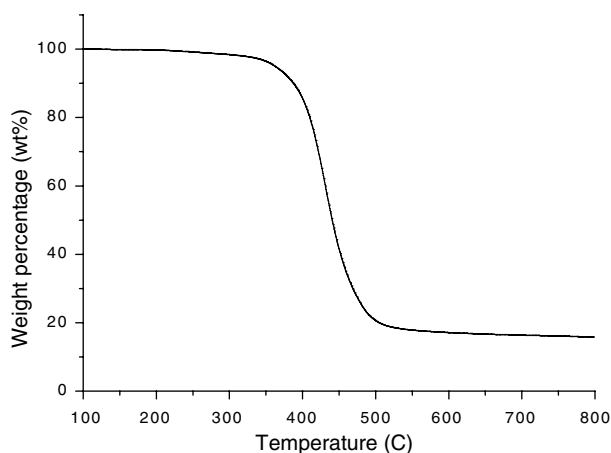
Fig. 1. TGA of TEOS/PVB hybrid film doped with Zn(TBP).
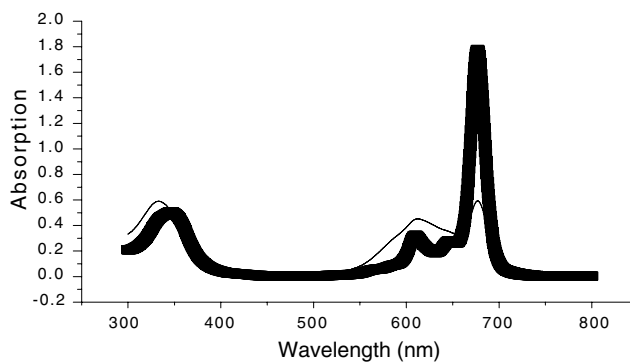
Fig. 2. UV–Vis spectra of CuPc(β-t-butyl)$_4$ in toluene and film: the thick line represents solution and the thin line represents film.
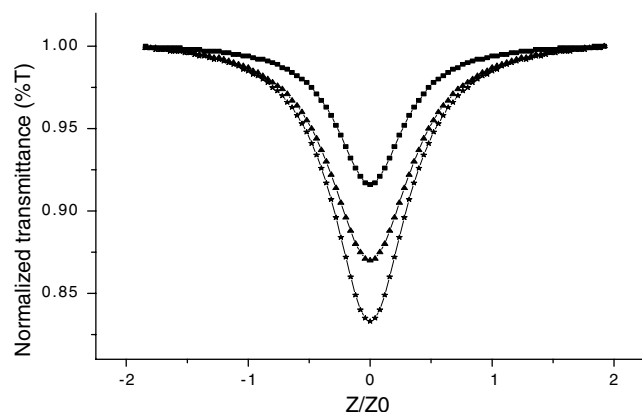
Fig. 3. Open aperture Z-scan results of CuPc in toluene at laser intensity of 1 μJ, rectangle represents CuPc(α-CP)$_4$, triangle represents CuPc(β-CP)$_4$ and star represents CuPc(β-t-butyl)$_4$, in each curve, and solid line for theoretical fits.
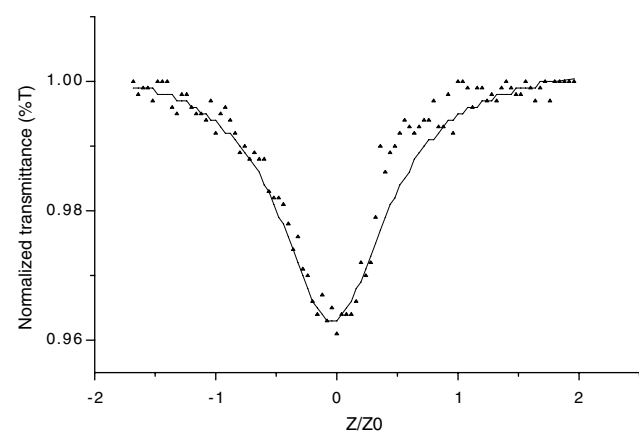

Fig. 4. Open aperture Z-scan results of CuPc(α-CP)$_4$ in sol–gel TEOS/PVB hybrid film. The input intensity is 1 μJ. Triangle represents experimental data and solid line for theoretical fits.

$$A \equiv \log \frac{1}{T} = \varepsilon Cl, \tag{3}$$

where ε is the proportional constant (extinction coefficient) and C is the concentration of sample. Eqs. (2) and (3) can be integrated to give $\alpha = 2.303\varepsilon C$. Finally, σ_{S0} can be obtained by Eq. (4).

$$\alpha = N_{S0}\sigma_{S0} = 6.02 \times 10^{23} \times \frac{C}{1000} \times \sigma_{S0}, \tag{4}$$

where N_{S0} represents molecular concentration of the ground state.

As shown in Table 1, all of the σ_{S1}/σ_{S0} ratios (a parameter to evaluate the limiting performance) for phthalocyanines in hybrid film and toluene are larger than one. This reveals that the absorption cross section of excited state for phthalocyanine is larger than that of ground state and phthalocyanine is exhibiting RSA properties. Therefore, the TEOS/PVB hybrid films doped with phthalocyanines are potential optical-limiting materials. However, the σ_{S1}/σ_{S0} ratios of phthalocyanines in hybrid films are lower than those in toluene. It is postulated that aggregation takes place in hybrid film doped with phthalocyanines. Aggregation causes intermolecular exciton coupling leading to lowering of the excited state cross-section in the hybrid film.

In toluene, CuPc(β-t-butyl)$_4$ exhibits the best optical-limiting effect among these dyes. In hybrid films, nevertheless, CuPc(α-CP)$_4$ exhibits highest σ_{S1}/σ_{S0} value than CuPc(β-t-butyl)$_4$ and CuPc(β-CP)$_4$. We surmise that the α-substitution with CuPc(α-CP)$_4$ has more serious steric hindrance and prevents the phthalocyanine ring from forming co-facial dimers or high-order aggregates.

3.3.2. RSA properties of porphyrins

Porphyrins usually exhibit two characteristic absorptions, which are Soret band (400–450 nm) and Q band (500–650 nm) [24], respectively. For instrumental consideration, we focused the region near 532 nm to investigate their RSA. We numerically fit the Z-scan results and obtain σ_{S1}/σ_{S0} ratios, as shown in Figs. 5–7, by the same method described in Section 3.3.1.

The σ_{S1}/σ_{S0} ratios of M(TBP) are summarized in Table 2. Experimental results reveal that all of σ_{S1}/σ_{S0} ratios for TEOS/PVB hybrid films doped with M(TBP) are larger than one except for Cu(TBP). Therefore, they are potential optical-limiting materials. Among them, the TEOS/PVB hybrid films doped with Zn(TBP) exhibits the strongest RSA properties and has the largest σ_{S1}/σ_{S0} ratio. We speculate that Cu(TBP) exhibits saturable absorption (SA) since it has strong absorption at 532 nm as shown in Fig. 8.

As shown in Table 2, however, the RSA properties of M(TBP) in sol–gel TEOS/PVB hybrid film and those in NMP (1-methyl-2-pyrrolidone) are quite different. Among lab-made M(TBP) in NMP, InCl(TBP) exhibits the strongest RSA properties and has the largest σ_{S1}/σ_{S0}

Table 1
The parameters for RSA of lab-made phthalocyanines in TEOS/PVB hybrid films and toluene

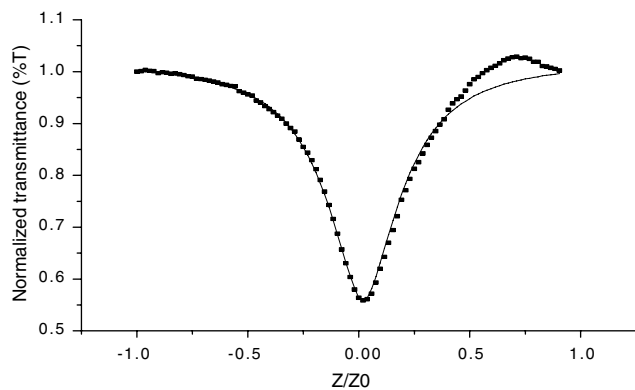| Compound	σ_{S0} (cm^2)		σ_{S1} (cm^2)		σ_{S1}/σ_{S0}	
	Toluene	Film	Toluene	Film	Toluene	Film
CuPc(α-CP)$_4$	4.0×10^{-18}	2.9×10^{-18}	6.9×10^{-17}	4.8×10^{-17}	17.3	3.9
CuPc(β-CP)$_4$	5.3×10^{-18}	7.6×10^{-18}	11.7×10^{-17}	2.3×10^{-17}	22.2	3.0
CuPc(β-t-butyl)$_4$	4.8×10^{-18}	1.2×10^{-17}	14.1×10^{-17}	3.1×10^{-17}	29.4	2.5

Fig. 5. Open aperture *Z*-scan results of Zn(TBP) in sol–gel TEOS/PVB hybrid film. The input 1 μJ. Rectangle represents experimental data and solid line for theoretical fits.
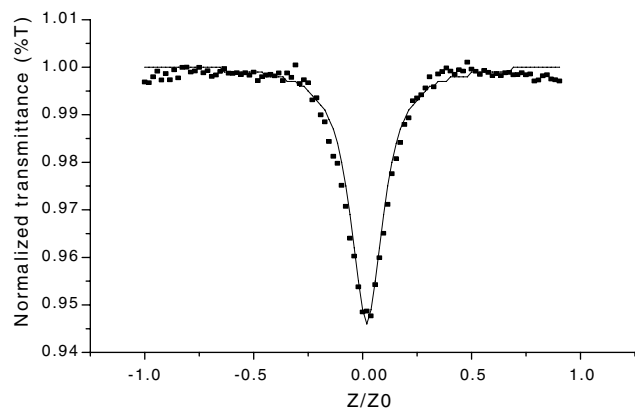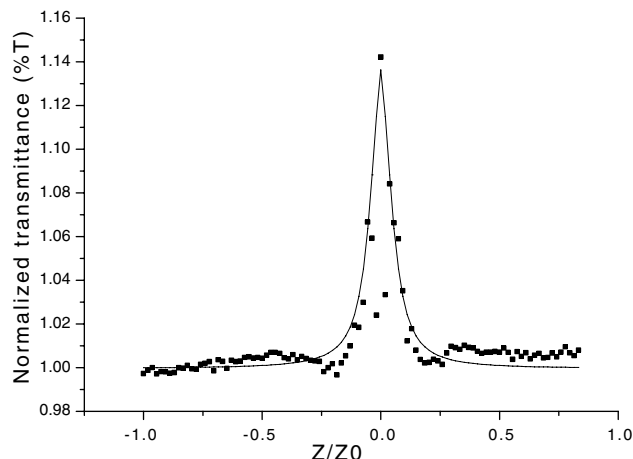

Fig. 7. Open aperture *Z*-scan results of Cu(TBP) in sol–gel TEOS/PVB hybrid film. The input intensity is 1 μJ. Rectangle represents experimental data and solid line for theoretical fits.
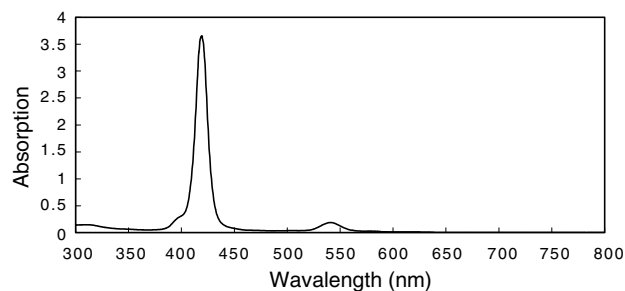

Fig. 6. Open aperture *Z*-scan results of InCl(TBP) in NMP. The input intensity is 1 μJ. Rectangle represents experimental data and solid line for theoretical fits.

Fig. 8. The UV/Vis spectrum of Cu(TBP) in sol–gel TEOS/PVB hybrid film.

ratio. It is notable that Cu(TBP) in NMP exhibits RSA rather than SA.

In sol–gel TEOS/PVB hybrid film, there seems to be no regularity for the RSA properties of M(TBP). However, in NMP, the σ_{S1}/σ_{S0} ratios depend on the atomic number of the central metal for M(TBP) due to heavy atom effect [25] so that InCl(TBP) exhibits the best RSA properties among lab-made M(TBP). Furthermore, the σ_{S1}/σ_{S0} ratios of metalloporphyrins are

larger than metal-free porphyrin. The exception is Cu(TBP) since its UV/Vis absorption locates near 532 nm, causing saturable absorption (SA) and decreasing its intrinsic RSA. In case of Cu(TBP) in sol–gel TEOS/PVB hybrid film, the SA surpasses the RSA. Thus, TEOS/PVB hybrid film doped with Cu(TBP) is not suitable for optical-limiting application with the laser of 532 nm as light source.

Compared with the RSA properties of phthalocyanines and porphyrins, we discover that phthalocyanines aggregate in sol–gel TEOS/PVB hybrid film, reducing their σ_{S1}/σ_{S0} ratios dramatically, as shown in Table 1.

Table 2
The parameters for RSA of lab-made M(TBP) in TEOS/PVB hybrid films and NMP (1-methyl-2-pyrrolidone)

Compound	σ_{S0} (cm²)		σ_{S1} (cm²)		σ_{S1}/σ_{S0}	
	NMP	Film	NMP	Film	NMP	Film
H₂(TBP)	2.33×10^{-17}	1.39×10^{-16}	3.7×10^{-17}	2.25×10^{-16}	1.6	1.62
Mg(TBP)	–	1.23×10^{-16}	–	1.5×10^{-16}	–	1.22
InCl(TBP)	4.21×10^{-17}	1.07×10^{-16}	2.9×10^{-16}	1.57×10^{-16}	7.81	1.5
Cu(TBP)	3.52×10^{-17}	3.5×10^{-17}	5.1×10^{-17}	2.3×10^{-17}	1.45	0.66
AlCl(TBP)	5.14×10^{-17}	–	2.9×10^{-16}	–	1.62	–
Zn(TBP)	4.21×10^{-17}	1.27×10^{-16}	8.4×10^{-17}	2.15×10^{-16}	2	1.7

Although porphyrins and phthalocyanines have analogous chemical structures, aggregation does not happen in case of porphyrins. Nevertheless, the σ_{S1}/σ_{S0} ratios of phthalocyanines in sol–gel TEOS/PVB hybrid film are 2–3 times larger than those of porphyrins. Thus, phthalocyanines are more suitable for optical limiting devices with 532 nm as laser source than porphyrins.

The RSA properties of phthalocyanines and porphyrins in TEOS/PVB are comparable to that in other solid matrix (polymethylmethacrylate (PMMA), epoxy resin, and chitosan, etc.) reported previously [26,27]. Furthermore, the organic–inorganic hybrids, dye/TEOS/PVB, exhibit excellent thermal resistance, flexibility, and feasibility for the industrial practicability in optical limiting devices.

4. Conclusion

Organic–inorganic TEOS/PVB hybrid films doped with phthalocyanines and porphyrins have been prepared. Their RSA properties in thin film have been investigated by *Z*-scan technique with picosecond laser pulse at 532 nm. The hybrid films doped with phthalocyanines are potential optical-limiting materials since they exhibit suitable σ_{S1}/σ_{S0} ratios and excellent thermal stability, increasing the industrial practicability in thin film fabrication for optical limiting devices.

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