

Synthesis and Optical Properties of Hyperbranched PAEKs Containing Porphyrin and Its Metal Derivatives^{*}

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Abstract Novel functional hyperbranched poly(aryl ether ketone)s (HPAEKs) bonded with nonlinear optical chromophores (meso-tetrakis(4-hydroxyphenyl) porphyrin, THPP and its metal derivatives) were synthesized and characterized by ¹H-NMR and UV-Vis absorption spectra. The incorporation of chromophores into HPAEKs endowed HPAEKs novel NLO and OL properties. Indeed, dendritic architecture allowed for maximum dispersion of the chromophores, avoided aggregation, more optical limiting property was obtained. Simultaneously, they retained the excellent properties of the materials, particularly in thermal stability. Their optical properties were evaluated by nonlinear optical analyses and optical limiting. The results showed that these polymers possessed good optical limiting (OL) property and large nonlinear optical (NLO) susceptibilities (*ca.* 10⁻¹² esu). All polymers containing chromophores presented excellent thermal stability (*DT*₅ > 524.17 °C).

Keywords: Porphyrin; Poly(aryl ether ketone)s; Hyperbranched; Optical limiting.

INTRODUCTION

In order to protect human eyes and sensitive optical systems from the lasers, the intensity of incoming laser must be reduced. Optical limiters are the materials which can reduce the intensity of hostile lasers by its instantaneous filtering action. The absorptive and refractive properties of the optical limiting material are altered by the incident laser light in such a manner that the resulting transmitted intensity is drastically reduced. Optical limiting materials based on reverse saturable absorption (RSA) are very useful for this purpose^[1].

Recently, several materials and device configurations have been proposed and developed to meet this challenge. Porphyrins as one of the promising candidates have been widely studied for their optical limiting property^[2–9]. A great number of structural changes consisting of the variation of the central atom and/or peripheral substituent groups at the pyrrolic free positions can be carried out in the porphyrins' structure without altering its chemical stability. The presence of an extended-electron system in porphyrin renders possible the verification of various nonlinear optical (NLO) effects. In porphyrins, the ground-state electronic absorption is mostly confined to a few narrow regions (Soret (–400 nm) and Q (–600 nm) bands), thus allowing high transmission in the spectral range comprised between these characteristic absorption bands^[10]. Porphyrins exhibit large excited-state absorption cross-sections, σ_{ex} , long triplet excited state times, τ , and high thermal and chemical stability^[11–14]. These properties afford porphyrins as interesting materials for the verification of effective optical limiting (OL)^[11].

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Poly(aryl ether ketone)s (PAEKs) are a class of important high-performance aromatic polymers which are used in the aerospace, electronics and nuclear fields^[15]. Excellent mechanical properties, thermal stability, electrical and chemical resistance properties make them a candidate for advanced materials^[16–17]. The incorporation of porphyrin units into the framework of the hyperbranched PAEKs (HPAEKs) can not only help to solve processing problems but also endow resultant polymers with novel properties. Retaining the excellent properties of the materials, particularly in thermal stability, preparation of the required NLO active materials for practical optical limiters is the focus research in the field.

Two families of highly branched macromolecules, dendrimers and hyperbranched polymers, have attracted considerable and increasing interest due to their fascinating unique structure, interesting and versatile performance and promising applications^[18–28]. In recent years, giant multiporphyrin dendritic arrays are obtained in time-consuming and tedious synthetic procedures, which make them costly for wide-range application^[29–32]. Hyperbranched multiporphyrin arrays possess architectures and properties similar to those of dendritic multiporphyrin arrays, but their synthesis is much simpler. Aggregation of porphyrin is generally adverse for optical limiting application since strong intermolecular interactions usually alter the excited state relaxation time and the effective nonlinear absorption of the material^[33]. Suppression of unfavorable aggregation is important to improve the optical limiting capability. The incorporation of chromophore units into the framework of hyperbranched PAEKs by covalent bond is of special interest since the dendritic architecture allows for maximum dispersion of the chromophores, a necessary condition for avoiding aggregation.

In this paper, the HPAEKs with porphyrin unit are successfully synthesized *via* direct polycondensation of 4, 4'-(hexafluoroisopropylidene)diphenol (6FBPA), meso-tetrakis(4-hydroxyphenyl)porphyrin (THPP) and 2, 2-bis(4-hydroxyphenyl)propane (BPA). And the corresponding metalloporphyrin polymers (Mg, Zn, Mn) are obtained. The NLO, OL properties and thermal performances of the polymers are discussed.

EXPERIMENTAL

Materials

4,4'-(Hexafluoroisopropylidene)diphenol (6FBPA) was purchased from Alfa Aesar. 4,4'-Difluorobenzophenone (DFB) was bought from Changzhou Huashan Chemical Co. Ltd. *N*-Methyl-2-pyrrolidone (NMP), chloroform (CHCl₃), dimethylformamide (DMF), 4-hydroxy benzaldehyde, pyrrole, MgCl₂·6H₂O, ZnCl₂ and MnCl₂·4H₂O were purchased from Shanghai Chemical Factory. All other reagents and solvents were obtained commercially and were purified by conventional methods. K₂CO₃ was dried at 120 °C for 24 h before polymerization.

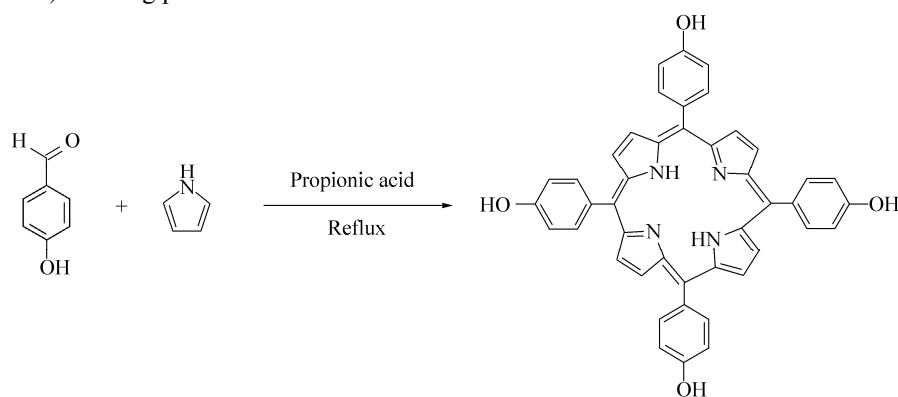
Characterization

A Bruker 510 instrument was used to record ¹H-NMR (500 MHz) spectra. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with *N,N*-dimethylformamide (DMF) as an eluent at a flow rate of 1 mL·min⁻¹. Glass transition temperatures (*T*_gs) were determined by DSC (Mettler Toledo DSC 821e) at a heating rate of 20 K·min⁻¹ under a nitrogen atmosphere. Thermo-gravimetric analysis was performed on a Perkin Elmer Pyris 1 TGA analyzer at a heating rate of 10 K·min⁻¹ under a nitrogen atmosphere. UV-Visible absorption spectra were recorded on a UV2501-PC spectrophotometer. The OL properties were measured in CHCl₃ solutions (5 mg·mL⁻¹). Testing was performed using a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd: YAG laser (EKSPLA PL2143B), which provided linearly polarized 21 ps optical pulses at 532 nm wavelength with a repetition of 5 Hz. The experimental arrangement was similar to that in the literature^[34]. The transverse mode of the laser pulses was nearly Gaussian. The input laser pulses were splitted into two beams by an attenuator (Newport). One was employed as reference to monitor the incident laser energy, and the other one was focused onto the sample cell by using a lens with 30 cm focal length. The sample was positioned at the focus and housed in quartz cells with a thickness of 2 mm. The incident and transmitted laser pulses were monitored by utilizing two energy detectors, D1 and D2 (Rjp-765 energy probes, Laser Precision). The NLO properties of the polymers were evaluated by a Z scan technique using the same laser system as that in the OL experiment. The experimental setup could be found in the literature^[35]. The

input energy was 340 μ J. The sample solution was placed in a 2 mm quartz cell and moved along the axis of the incident beam (*z*-direction).

Synthesis of Meso-tetrakis(4-hydroxyphenyl)porphyrin (THPP)

THPP was synthesized according to the literature^[36] (Scheme 1). 4-Hydroxy benzaldehyde (9.159 g, 75 mmol) was dissolved in 500 mL propionic acid. The solution was heated to 140 °C. A volume of newly distilled pyrrole (5.19 mL, 75 mmol) was added slowly, the mixture was refluxed for 1 h, followed by the addition of 500 mL anhydrous alcohol. The solution was transferred into a big beaker, cooled to room temperature and placed for 10 h at −20 °C, then, filtered, and the filter cake was washed thoroughly with the mixture of propionic acid and alcohol (*V/V* = 1:1) and CHCl₃, respectively. The obtained blue powder was dissolved with anhydrous alcohol and the solution was recrystallized to obtain violet solid of THPP. The reaction yield was 10%. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS): *m/z* = 678.5. ¹H-NMR (acetone-*d*₆, δ): 8.95 (s, 8H, β -Pyrrole), 8.89 (s, 4H, −OH), 8.08 (d, 8H, 2, 6-phenyl), 7.31 (d, 8H, 3, 5-Phenyl), −2.67 (s, 2H, NH-pyrrole). IR (KBr, cm^{−1}): 3433 (OH), 3356, 1089 (NH), 3024, 2974 (CH−Ar), 1610, 1506.5 (−C=C−Ar), 1237 (C−O), 1068 (CH−pyrrole). λ_{max} (C₂H₅OH): 418.5 nm (Soret Band), 516, 554, 595, 650 nm (Q Bands). Melting point: 422.75 °C.



Scheme 1 Synthetic scheme of THPP

Polymerization

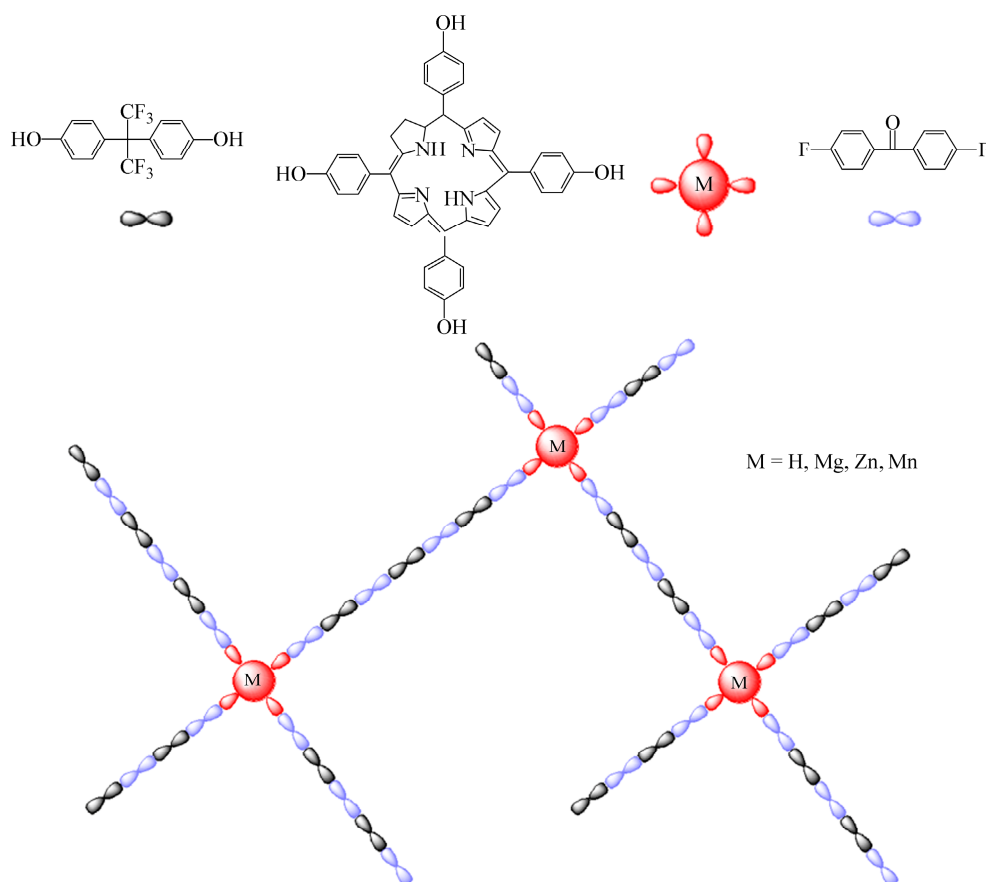
Synthesis of hyperbranched poly(arylene ether ketone)s containing porphyrin (HPAEK)

6FBPA, THPP, DFB, K₂CO₃, DMF and toluene were added into a 50 mL three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, a thermometer and a nitrogen inlet. Under nitrogen atmosphere, the mixture was heated to 128 °C, maintained at that temperature for 3 h to dehydrate by means of a Dean-Stark trap through toluene. The reactions of polymerization are shown in Scheme 2. The nonlinear optical chromophores (THPP and its metal derivatives) bonded to the framework of HPAEKs, dendritic architecture allowed for maximum dispersion of the chromophores, avoided aggregation. After dehydration and removal of toluene, the condensation polymerization was continued for 4 h at 150 °C. Then, the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized, the resulted powders were washed several times with hot deionized water and ethanol, then dried at 120 °C under vacuum for 24 h. (yield: 95%) The detail reaction conditions and results of polymerization of HPAEKs could be found in Table 1.

Table 1. Reaction conditions and results of polymerization of HPAEKs

Samples	THPP:6FBPA:DFB (mol ratio)	OH:F (mol ratio)	M_n (10 ³ g·mol ^{−1})	M_w (10 ³ mol·g ^{−1})	PDI	porphyrin ^a (%)
HPAEK-1%	1:99:100	1.03:1	13.4	37.5	2.8	0.83
HPAEK-3%	3:97:100	1.09:1	15.5	51.2	3.3	2.56
HPAEK-5%	5:95:100	1.15:1	19.3	79.1	4.1	4.42

^a The percentage content of porphyrin in porphyrin and 6FBPA (mol ratio, calculated from the ¹H-NMR spectrum)



Scheme 2 Synthetic scheme of HPAEKs containing porphyrin and its metal derivatives

Synthesis of hyperbranched poly(arylene ether ketone)s containing metalloporphyrin (M-HPAEK)

HPAEK and excesses metal chlorides ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 or $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were added into a 100 mL three-necked flask equipped with a condenser, and the mixed solvent of CHCl_3 and DMF ($V/V = 1:1$) was then added. Under nitrogen atmosphere, the mixture was refluxed for 2 h. Then, the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized into powders. The resulted powders were washed several times with hot deionized water and ethanol, and then dried at 120 °C under vacuum for 24 h. M-HPAEKs were successfully prepared (yield: 96 %).

RESULTS AND DISCUSSION

Structure Characterization

All the polymers were well characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained. The structures of the synthesized polymers were confirmed by ^1H -NMR spectra. Figure 1 shows the ^1H -NMR spectra of (A) HPAEK-1%, (B) HPAEK-3% and (C) HPAEK-5%. The chemical shifts from $\delta = 7.78$ to 7.88 were assigned to benzene protons in the ortho position of ketone bonds while the spectrum showed the NH-pyrrole proton at $\delta = -2.74$.

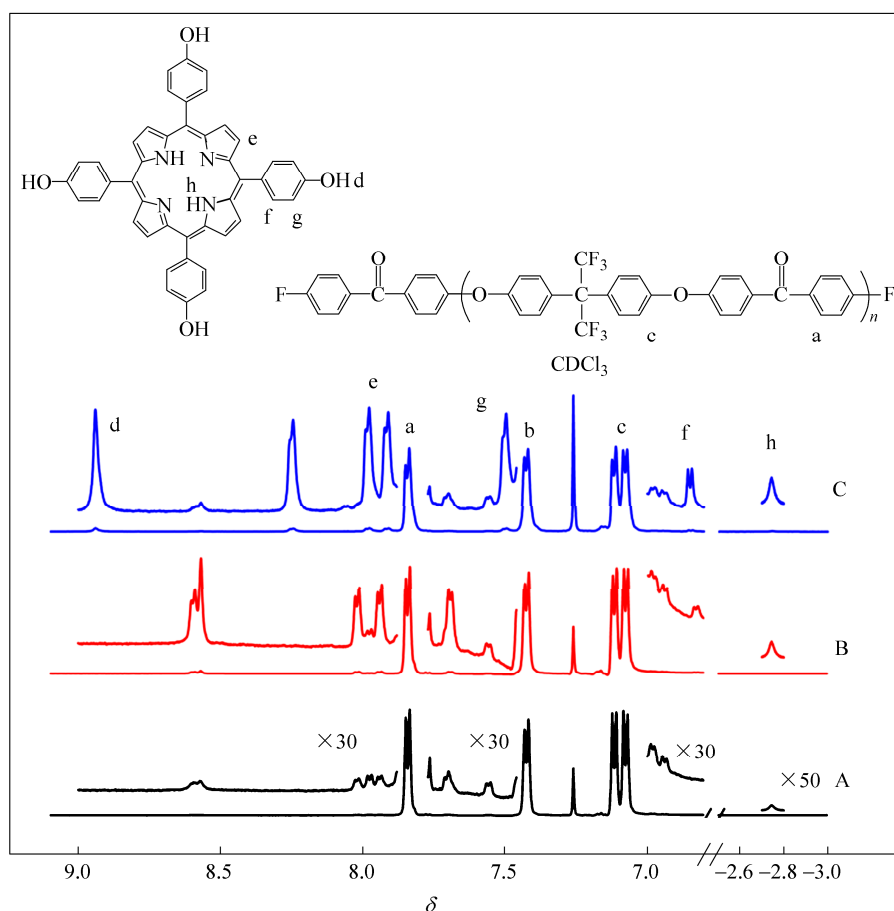


Fig. 1 ^1H -NMR spectra of (A) HPAEK-1%, (B) HPAEK-3% and (C) HPAEK-5% in chloroform-d

The ^1H -NMR spectrum was also used to determine the THPP content in the polymer. Provided that x represented the peak area of one proton of the NH-pyrrole segment and y was the peak area of one proton of the benzene in the ortho position of ketone bonds segment. The content of the THPP segment might be estimated by directly comparing the peak area of all NH-pyrrole protons with the peak area of benzene protons in the ortho position of ketone bonds based on the following equation:

$$2x:4y = A_{\text{NH}}:A_{\text{Ar}} \quad (1)$$

where A_{NH} corresponded to the absorption peak area of all NH-pyrrole protons of the polymer. A_{Ar} was associated with the peak areas of all benzene protons in the ortho position of ketone bonds. Thus, the THPP content in the polymer could be calculated according to Eq. (1):

$$\text{The THPP content (mol\%)} = x/(x + y) \times 100\% = 2A_{\text{NH}}/(2A_{\text{NH}} + A_{\text{Ar}})$$

The THPP contents in HPAEK-1%, HPAEK-3% and HPAEK-5% were calculated to be 0.83%, 2.56% and 4.42%, respectively.

The UV-Vis spectra of the polymers in chloroform are shown in Fig. 2. The backbone absorption of HPAEKs was found at 291 nm. M-HPAEKs coordinated with different metals, exhibited different Soret and Q bands. The polymers had the similar structure in every series, but the content of nonlinear optical chromophores (THPP and its metal derivatives) was different. Their UV-Vis spectra would be the same.

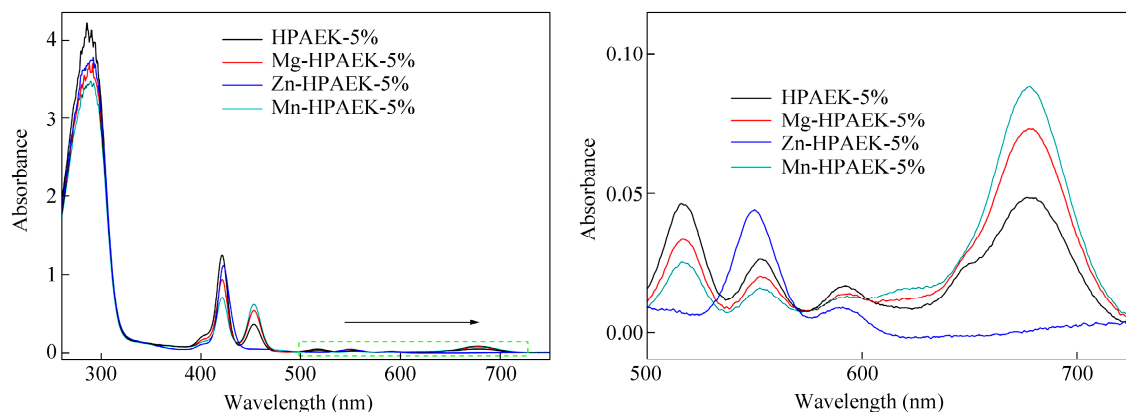


Fig. 2 UV-Vis spectra of chloroform solutions of HPAEK-5%, Mg-HPAEK-5%, Zn-HPAEK-5% and Mn-HPAEK-5%

Take the polymer-5% of every series for example, the data are listed in Table 2. HPAEK-5%, Mg-HPAEK-5% and Mn-HPAEK-5% exhibited absorption at the same wavelengths. But, the absorption intensity of different samples changed. The absorption intensity order was HPAEK-5% > Mg-HPAEK-5% > Mn-HPAEK-5% at the wavelength 453 nm and 561 nm. While at 678 nm, the absorption intensity order changed into Mn-HPAEK-5% > Mg-HPAEK-5% > HPAEK-5%.

Table 2. The UV-Vis absorption wavelengths of polymers

Samples	Backbone (nm)	Soret band (nm)	Q bands (nm)
HPAEK-5%	291	421.5	453, 561.5, 553.5, 592, 678
Mg-HPAEK-5%	291	421.5	453, 561.5, 553.5, 592, 678
Zn-HPAEK-5%	291	422.5	550, 592
Mn-HPAEK-5%	291	421.5	453, 561.5, 553.5, 592, 678

Thermal Properties

The glass transition temperatures (T_g s) and TGA data of the polymer are listed in Table 3. The data indicated that the T_g values of HPAEKs showed some orderliness. T_g s of the HPAEKs containing more THPP were slightly higher than those of the other polymers. The higher THPP content, the higher T_g s was. THPP as a rigid unit linked to the polymers, causing the T_g s of polymers to rise. The T_g s of M-HPAEKs distributed from 161 °C to 164 °C.

Table 3. Thermal properties of polymers

Samples	T_g^a (°C)	DT_5^b (°C)	DT_{10}^c (°C)
HPAEK-1%	156	559	574
HPAEK-3%	164	561	578
HPAEK-5%	165	564	581
Mg-HPAEK-1%	161	526	543
Mg-HPAEK-3%	161	533	552
Mg-HPAEK-5%	162	530	548
Zn-HPAEK-1%	161	524	540
Zn-HPAEK-3%	163	544	563
Zn-HPAEK-5%	163	528	546
Mn-HPAEK-1%	163	537	553
Mn-HPAEK-3%	164	533	551
Mn-HPAEK-5%	164	537	556

^a From the second heating trace of DSC measurements conducted at a heating rate of 20 K·min⁻¹.

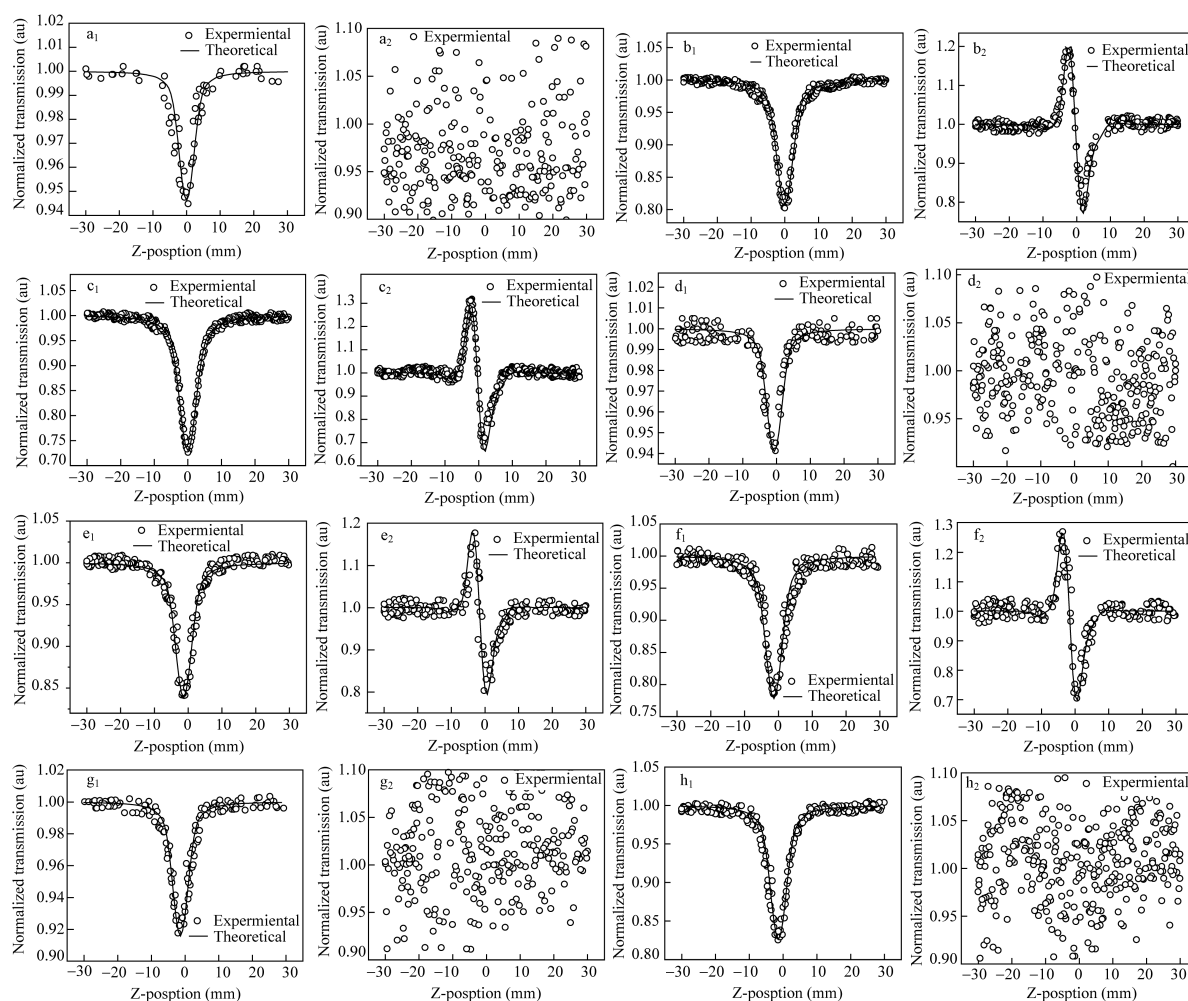
^b 5% weight loss temperatures measured by TGA at a heating rate of 10 K·min⁻¹ in N₂.

^c 10% weight loss temperatures measured by TGA at a heating rate of 10 K·min⁻¹ in N₂.

The thermal stability of the polymers was vital to their applications in optical limiting. To examine the thermal durability of these polymers, several thermogravimetric (TGA) experiments were performed under N_2 atmosphere. As shown in Table 3, HPAEK series, the TGA data (DT_5 and DT_{10}) of the polymers containing more THPP were higher than those of the other polymers. THPP as a rigid unit had high thermal stability, incorporated into the framework of HPAEKs by covalent bond, exhibited excellent thermal stability. The DT_5 of M-HPAEKs ranged from 524 °C to 544 °C, while DT_{10} ranged from 540 °C to 563 °C, slightly lower than those of HPAEK series. THPP and M-THPP as rigid unit had high thermal stability, also, they could accelerate the degradation of the polymers under heating in N_2 atmosphere. M-THPP was of stronger catalytic ability than THPP, THPP coordinated with different metals exhibited different catalytic ability. Under the influence of these two factors, DT_5 and DT_{10} of M-HPAEKs showed irregular changes with the increases of M-THPP. Above all, all polymers presented excellent thermal properties.

Nonlinear Optical Property

The nonlinear absorption coefficients of the polymers were measured by Z scan technique. The results of Z scan with and without an aperture showed that all the polymers had both nonlinear absorption and refraction. Thus, the $\chi^{(3)}$ of the polymers should be dually attributed to nonlinear absorption (α_2) and refractive index (n_2) of the molecules. The Z scan results of the polymers are shown exemplarily in Fig. 3.



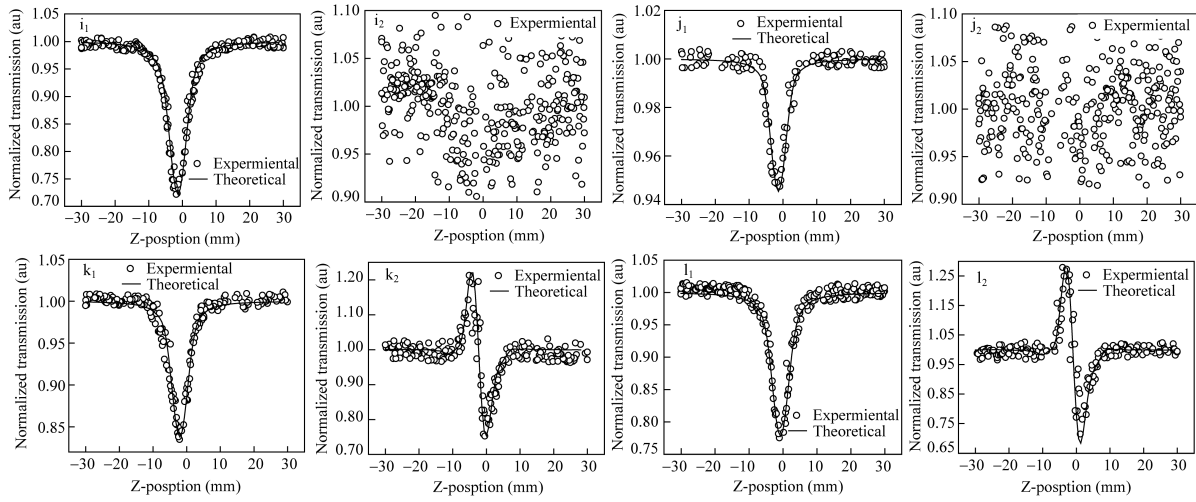


Fig. 3 Z-scan data of (a) – (c) HPAEK-1%, 3%, 5%, (d) – (f) Mg-HPAEK-1%, 3%, 5%, (g) – (i) Zn-HPAEK-1%, 3%, 5%, and (j) – (l) Mn-HPAEK-1%, 3%, 5% (5 mg·mL⁻¹); (a₁) – (i₁) with open aperture and (a₂) – (i₂) with closed aperture

In theory, the normalized transmittance for the open aperture can be written as^[37, 39]

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1 \quad (2)$$

where $q_0(z) = \alpha_2 I_0(t) L_{\text{eff}} / (1 + z^2/z_0^2)$; α_2 was nonlinear absorption coefficient; $I_0(t)$, intensity of laser beam at focus ($z = 0$); $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)] / \alpha_0$ was the effective thickness with α_0 , linear absorption coefficient; L , sample thickness; z_0 , diffraction length of the beam, and z , sample position. Thus, the nonlinear absorption coefficients of the polymers could be determined by fitting the experimental data using Eq. (2). The nonlinear refractive index n_2 was given by^[38, 39]

$$n_2 = \frac{\lambda \alpha_0}{2\pi I_0 (1 - e^{-\alpha_0 L})} \frac{\Delta T_{p-v}}{0.416(1-S)^{0.25}} \quad (3)$$

where ΔT_{p-v} was the difference between the normalized transmittance values at the valley and peak portions and S was the aperture size ($S = 0.12$). Thus, the nonlinear refractive coefficients of the polymers could be determined by using Eq. (3). The $\chi^{(3)}$ can be calculated by the following equation^[37, 38]

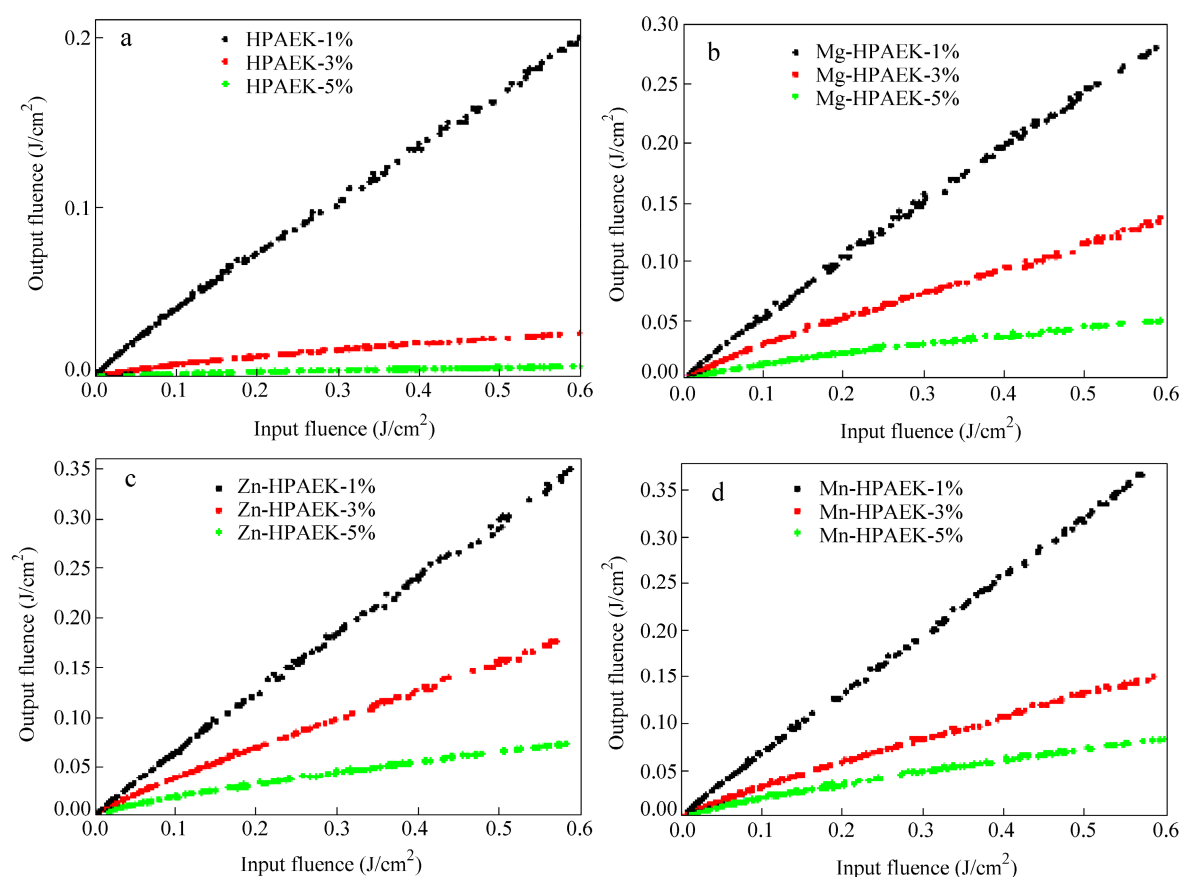
$$|\chi^{(3)}| = \sqrt{\left| \frac{cn_0^2}{80\pi} n_2 \right|^2 + \left| \frac{9 \times 10^8 \varepsilon_0 n_0^2 c^2}{4\pi\omega} \alpha_2 \right|^2} \quad (4)$$

where ε_0 , permittivity of vacuum; c , speed of light; n_0 , refractive index of the medium, and $\omega = 2\pi/\lambda$.

The calculation results of the nonlinear optical coefficients of the four polymers are displayed in Table 4. It was well known that PAEKs did not have nonlinear optical values. But, the nonlinear susceptibilities of the polymers containing nonlinear optical chromophores reached *ca.* 10⁻¹² esu. The incorporation of chromophores into the HPAEKs endowed the resultant polymers with novel NLO properties. The NLO properties were affected by the amount of chromophores in the polymers, and the solutions with high percent chromophores exhibited better performances.

Table 4. Properties of the polymers

Polymer ^a	Transmittance	Limiting threshold ^b (J/cm ²)	Limiting amplitude ^c (J/cm ²)	Nonlinear optical values ^d		
				α_2 (m/W)	n_2 (m/W)	$\chi^{(3)}$ (esu)
HPAEK-1%	93%	0.139	0.201	1.5×10^{-12}	—	0.05×10^{-12}
HPAEK-3%	59%	0.056	0.026	3.6×10^{-11}	-2.9×10^{-18}	2.53×10^{-12}
HPAEK-5%	42%	0.032	0.006	6.9×10^{-11}	-5.7×10^{-18}	4.96×10^{-12}
Mg-HPAEK-1%	80%	0.127	0.280	6.2×10^{-12}	—	0.20×10^{-12}
Mg-HPAEK-3%	61%	0.109	0.134	2.0×10^{-11}	-1.8×10^{-18}	1.54×10^{-12}
Mg-HPAEK-5%	53%	0.063	0.052	3.3×10^{-11}	-3.1×10^{-18}	2.63×10^{-12}
Zn-HPAEK-1%	82%	0.230	0.347	0.8×10^{-11}	—	0.26×10^{-12}
Zn-HPAEK-3%	69%	0.100	0.180	2.1×10^{-11}	—	0.69×10^{-12}
Zn-HPAEK-5%	56%	0.061	0.073	4.6×10^{-11}	—	1.51×10^{-12}
Mn-HPAEK-1%	79%	0.163	0.365	0.5×10^{-11}	—	0.16×10^{-12}
Mn-HPAEK-3%	62%	0.120	0.150	2.0×10^{-11}	-2.2×10^{-18}	1.82×10^{-12}
Mn-HPAEK-5%	49%	0.094	0.085	3.4×10^{-11}	-3.4×10^{-18}	2.86×10^{-12}

^a The concentration of the polymers was 5 mg·mL⁻¹ in CHCl₃^b Incident fluence at which the output fluence started to deviate from linearity^c Maximum output intensity^d Measured by Z scan technique with an 21 ps Nd: YAG laser system at 5 Hz repetition rate and 532 nm wavelength**Fig. 4** (a), (b), (c) and (d) optical responses to 21 ps, 5 Hz pulses of 532 nm laser light of CHCl₃ solutions of HPAEK-1%, 3%, 5%, Mg-HPAEK-1%, 3%, 5%, Zn-HPAEK-1%, 3%, 5% and Mn-HPAEK-1%, 3%, 5% (5 mg·mL⁻¹)

Optical Limiting Property

Figure 4 shows the optical limiting performances of polymers containing chromophores at the same concentration ($5 \text{ mg}\cdot\text{mL}^{-1}$ in CHCl_3). As shown in Fig. 4, at low incident fluence, the output fluence of the polymer solutions linearly increased with the incident fluence obeying the Lambert-Beer law. However, at high incident fluence, the transmittance of the solution decreased, and a nonlinear relationship was observed between the output and input fluences, with a further increase in the incident fluence, the transmitted fluence reached a plateau (limiting amplitude), showing the good optical limiting property.

Take HPAEK-1% for example, the transmitted fluence of HPAEK-1% solution increased linearly with the incident fluence but started to deviate at a value of $0.139 \text{ J}/\text{cm}^2$ (defined as the limiting threshold, that is, the incident fluence at which the output fluence starts to deviate from linearity). When the incident fluence increased to $0.6 \text{ J}/\text{cm}^2$, the transmitted fluence was saturated at $0.201 \text{ J}/\text{cm}^2$ (defined as the limiting amplitude, that is, the maximum output intensity). The results of the other polymers are summarized in Table 4. The limiting threshold of the polymers decreased from 0.139 to $0.032 \text{ J}/\text{cm}^2$, while the limiting amplitude changed from 0.201 to $0.006 \text{ J}/\text{cm}^2$ when the sample changed from HPAEK-1% (THPP, 0.83%), HPAEK-3% (THPP, 2.56%) to HPAEK-5% (THPP, 4.42%). THPP acts as nonlinear optical chromophores bonded to the polymer, more THPP should absorb more energy of the harsh laser. The incorporation of THPP units into the framework of HPAEKs made THPP disperse well in the polymer, avoided aggregation, more optical limiting property was obtained. Also, the similar results could be found in Mg-HPAEK, Zn-HPAEK and Mn-HPAEK series. They all exhibited good optical limiting property.

CONCLUSIONS

Four series of novel functional hyperbranched multiporphyrin arrays bonding nonlinear optical chromophores (THPP and its metal derivatives) were successfully synthesized in high yield. The incorporation of chromophores into HPAEKs endowed HPAEKs novel NLO and OL properties. Indeed, dendritic architecture allowed for maximum dispersion of the chromophores, avoided aggregation, more optical limiting property was obtained. Simultaneously, they retained the excellent properties of the materials, particularly the thermal stability. Their NLO and OL properties were investigated by a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd: YAG laser, which provided linearly polarized 21 ps optical pulses at 532 nm wavelength with a repetition of 5 Hz. These studies have shown that the polymers exhibited good optical limiting (OL) and large nonlinear optical (NLO) susceptibilities (*ca.* 10^{-12} esu). All polymers containing chromophores presented excellent thermal stability ($DT_5 > 524^\circ\text{C}$). This work provided a novel path for designing new optical materials with good optical limiting property.

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