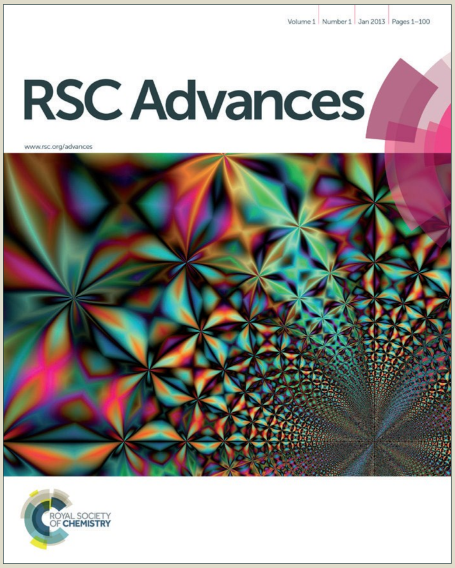
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Poly(arylene ether ketone)s with Pendant Porphyrins: Synthesis and Investigation on Optical Limiting Properties

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yinlong Du,[a] Kai Zhu,[a] Yu Fang,[b] Shuling Zhang,[a] Xingrui Zhang,[a] Yaning Lu,[a] Yanchao Yang,[a] Yinglin Song,[b] and Guibin Wang*[a]

This paper describes the synthesis and characterization of a novel series of poly(arylene ether ketone)s bearing porphyrin pendants, along with the demonstration of their nonlinear optical and optical limiting properties at 532 nm in both THF and films. The incorporation of pendant porphyrins was done through a modified esterification using a copoly(arylene ether ketone) with free carboxyl groups and mono-hydroxyphenyl porphyrins with different substituents and center metal. The introduction of porphyrin in the polymer was confirmed by IR, ^{1}H NMR, UV-vis, fluorescence spectroscopies, and WAXD. Investigation of thermal properties indicated that the poly(arylene ether ketone)s with porphyrin pendants possessed higher T_gs, and slightly lower decomposition temperatures than the starting copolymers. The results of optical limiting and *Z*-scan measurements demonstrated that the porphyrinated poly(arylene ether ketone)s exhibited strong optical limiting responses and nonlinear absorption properties with the nonlinear absorption coefficient β in the order of 10^{-9} (m W^{-1}) magnitude. The effects of pendant porphyrin structure on the thermal, mechanical, linear and nonlinear optical properties of the poly(arylene ether ketone)s were investigated in detail.

Introduction

The rapid advance of laser technology injects new opportunities into the photonic, medical, and military applications, as well as the development of nonlinear optical (NLO) materials and devices for applications such as optical data storage, information process, and optical limiting.[1-3] Within the scope of nonlinear optics, optical limiting (OL) materials which effectively attenuate damaging laser pulses for protecting delicate optical sensors and human eyes from exposure to intense light beams, while exhibit high transmittance for low intensity ambient light have been extensively investigated.[4-6] In general, the performance specifications for an ideal optical limiter require fast response time, Broad-band spectral response range, large nonlinearities, low limiting threshold, and high linear transmittance in the absence of intense light.[7,8] Furthermore, ease of processing, good mechanical strength and thermal stabilities are also necessary for practical applications of OL materials.

Among the widely investigated materials for optical limiting, organic compounds with extended π conjugated systems such as porphyrins and phthalocyanines have exhibited superior optical limiting properties due to the occurrence of reverse saturable absorption (RSA) process, which involves an excited state absorption with cross section (σ_{ex}) exceeding that of the ground state absorption (σ_0) under photoexcitation.[9,10] Porphyrins have been the most intensively studied NLO compounds since their RSA effect was first reported by Blau et al.[11] The structural changes consisting of the variation of peripheral substituents, central metals, and the type of axial ligands give rise to their adjustable optical properties, rendering porphyrins still among the most promising materials toward optical limiting.[9,10,12] As it is difficult to fabricate optical devices with single porphyrin molecule or solution, a variety of polymers have been selected as solid state matrices over the past decades. However, the direct introduction of porphyrins into polymers usually bring about aggregation and poor dispersion, resulting in undesirable performance. To solve these problems, previous efforts have been devoted to the design and preparation of porphyrin polymers by covalent attachment for the purpose of photovoltaic,[13,14] electrospinning,[15,16] nonlinear optics,[17,18] semiconducting,[19] gas storage,[20,21] and photosensitizer.[22] Up to now, in spite of the wide variety of polymers that incorporate porphyrin units, few of them have been considered as an ideal material capable of protecting delicate optical devices due to their inferior thermal stabilities and corrosion resistance, which make them vulnerable to high energy density laser. In view of this issue, it is critically important to explore and evaluate high performance (especially good thermal resistance) polymers in the field of NLO materials.

Poly(arylene ether ketone)s (PAEKs) are an important species of high performance thermoplastics characterized by their outstanding chemical, nonflammable, thermal, and mechanical properties.[23-26] The semi-crystalline nature, poor solubility, and low glass transition temperature of the original poly(ether ether ketone) have been improved by means of modifying molecular segment structure.[27-30] Currently, this class of advanced materials is receiving extensive attention for potential applications on fiber reinforced composites,[31,32] proton/anion exchange membrane,[33-37] and low dielectric constant materials.[38,39] However, synthesis and properties of PAEKs incorporating NLO chromophores have scarcely been reported. Since PAEKs combine rigidity, flexibility and good thermal resistance, we expect them to be promising substituents for poly(methyl methacrylate) as optical limiting materials.[40,41]

This work reports the synthesis and characterization of poly(arylene ether ketone)s having porphyrin pendant units anchored at the sidechains via a flexible alkyl chain, along with their optical properties, thermal stabilities, and mechanical properties. To avoid the complicated procedures of synthesizing the corresponding porphyrin monomer and its possible low reactivity as a bulky bisphenol monomer, the introduction of porphyrin pendant groups was achieved through *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) catalyzed esterification reactions using a poly(arylene ether ketone) with free carboxyl groups and asymmetric mono-hydroxyphenyl porphyrins. Their optical limiting properties were evaluated by *Z*-scan and optical limiting measurements. Furthermore, the influence factors, such as content, central metal, and peripheral substituent of porphyrin moieties on the optical and thermal properties of the polymers were comparatively investigated.

Experimental Section

Materials

1-Napthaldehyde (95%), p-tolualdehyde (97%) and 4,4'-(hexafluoroisopropylidene) diphenol (97%, mp 160-163 ^{o}C) were purchased from Sigma-Aldrich Chemical Componay. 4-Hydroxy benzaldehyde (98%), benzaldehyde (98%), and pyrrole (98%) were purchased from Shanghai Chemical Factory and were distilled prior to use. Diphenolic Acid (98%) was provided by TCI Shanghai Development Co. Ltd., China. 4,4'-Difluorobenzophenone (DFB) was obtained from Changzhou Huashan Chemical, China and further purified by recrystallization. *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) were supplied by Sigma-Aldrich. Zinc acetate dihydrate ($Zn(OAc)_2\cdot 2H_2O$) and lead acetate trihydrate ($Pb(OAc)_2\cdot 3H_2O$) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Tetrahydrofuran (THF) and *N*-Methyl-2-pyrrolidinone (NMP) were distilled according to standard procedures before use.

Instruments.

FTIR spectra (KBr pellets) were recorded on a Nicolet Impact 410 Fourier transform infrared spectrophotometer in transmission. ^{1}H NMR was recorded on a Bruker 510 NMR spectrometer (500 MHz) in $CDCl_3$ with tetramethylsilane as a reference. Mass spectra (MS) were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min^{-1}. The crystallization behavior was investigated by Rigaku D/max-2500 X-ray diffractometer with CuKα radiation (λ=0.154 nm) as the X-ray source. Energy dispersive spectroscopic (EDS) data was collected on Nova Nano (FEI) scanning electron microscope (SEM) 450 equipped with energy dispersive spectroscopy. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 821e instrument at a heating rate of 20 ^{o}C min^{-1} under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA analyzer; the samples were contained in open platinum pans at a heating rate of 10 ^{o}C min^{-1} under nitrogen. UV-vis absorption and fluorescence emission spectra were recorded on a UV2501-PC spectrophotometer and Shimadzu RF-3501 fluorescence spectrophotometer, respectively. The mechanical properties of polymer films (rectangular films of 45.0 (length) × 5.0 (width) × 0.1 (thickness) mm^3, cast from THF solvents onto the glass plates, followed by heating at 60 ^{o}C in vacuo), were evaluated at room temperature at a strain rate of 10 mm min^{-1} on a Shimadzu AG-I Universal Tester, and each film was measured five times in parallel.

The nonlinear optical (NLO) properties of the samples were evaluated by *Z*-scan technique using a Q-swithced ns Nd:YAG laser system continuum with linearly polarized 4 ns pulsed light at 10 Hz repetition rate and 532 nm wavelength. THF solution of polymers was placed in a quartz cell with a thickness of 2 mm and placed at the focal point of a lens with a focal length of 40 cm, and moved along the axis of the incident beam (*z* direction). The measurements were carried out employing open-aperture and closed-aperture configurations with the input energy of 5.3μJ. The incident and transmitted laser pulses were monitored by utilizing two energy detectors, D1 and D2 (Rjp-765 energy probes, Laser Precision), which were linked to an energy meter (Rj-7620 Energy Ratiometer, Laser Probe Inc.). A computer was used to process the data coming from the energy meter via a GPIB interface. The optical limiting properties were performed using *Z*-scan technique with the same laser system as in the nonlinear absorption experiments, where the intensity of the incident energy is varied continuously and the output energy is captured by a large aperture photodetector kept at a distance of 10 cm from the samples; The samples were positioned in a quartz cell of 5 mm thickness at the focal point, and curves of output energy or transmittance vs input energy were obtained.

Synthesis of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin.

This compound was synthesized by Adler's method.[42] The crude product was purified by silica-gel column chromatography using $CHCl_3$ as eluent to collect the second fraction, then the solvent was evaporated and dried to yield bright purple crystalline, 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (OH-TPP) (yield: 6.2%). IR (KBr): ν_{max} (cm^{-1}): 3408 (OH), 3314 (NH), 1607, 1510 (Ar), 1169 (Ar-O), 799 (Ar). ^{1}H NMR (500 MHz, $CDCl_3$, TMS), δ(ppm): 8.86 (s, 8H, pyrrolic-β-CH), 8.19-8.21 (m, 6H, *ortho*-C_6H_5), 8.04-8.06 (d, 2H, J = 8.5 Hz, *ortho*-C_6H_4OH), 7.73-7.75 (m, 9H, *meta, para*-C_6H_5), 7.13-7.16 (d, 2H, J = 8.5 Hz, *meta*-C_6H_4OH), -2.78 (s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, TMS), δ(ppm): 146.84, 145.89, 142.22, 140.46, 138.83, 135.63, 134.52, 129.98, 128.35, 127.80, 127.74, 127.65, 126.67, 126.63, 115.25, 113.63. MALDI-TOF MS: calculated for ($C_{44}H_{30}N_4O$): *m/z* $[M + H]^+$: 631.25; found: *m/z* = 631.6.

Synthesis of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin.

Following a similar procedure to the preparation of OH-TPP, 4-hydroxybenzaldehyde (3.053 g, 25 mmol), p-tolualdehyde (9.011 g, 75 mmol) and pyrrole (6.8 mL, 100 mmol) was added dropwise to 300 mL propionic acid in 30 min with stirring at 140 °C. The mixture was refluxed for 1 h, most of propionic acid was removed under reduced pressure. The dark purple product was filtered and washed thoroughly with methanol until the filtrate became clear and the crude product was purified through column chromatography ($CHCl_3$). The second fraction was collected and evaporated to give 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (OH-TTP) (yield: 5.7%). Anal. Calcd for ($C_{47}H_{36}N_4O$): C 83.90, H 5.39, N 8.33. Found: C 83.93, H 5.47, N 8.35%. IR (KBr): v_{max} (cm^{-1}): 3423 (OH), 3312 (NH), 2935 (CH_3), 1603, 1507 (Ar), 1159 (Ar-O), 801 (Ar). ^{1}H NMR (500 MHz, $CDCl_3$, TMS), δ(ppm): 8.85 (s, 8H, pyrrolic-β-CH), 8.07-8.10 (d, 6H, J = 7.9 Hz, *ortho*-C_7H_7), 8.01-8.04 (d, 2H, J = 8.5 Hz, *ortho*-C_6H_4OH), 7.53-7.55 (d, 6H, J = 7.9 Hz, *meta*-C_7H_7), 7.10-7.13 (d, 2H, J = 8.5 Hz, *meta*-C_6H_4OH), 2.69 (s, 9H, CH_3), -2.78 (s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, TMS), δ(ppm): 146.65, 146.32, 145.81, 140.44, 139.35, 138.89, 137.31, 135.61, 134.51, 130.99, 129.24, 128.03, 127.73, 127.39, 120.09, 113.62, 21.48. MALDI-TOF MS: calculated for ($C_{47}H_{36}N_4O$): *m/z* $[M + H]^+$ = 673.29; found: *m/z* = 673.4.

Synthesis of 5-(4-hydroxyphenyl)-10,15,20-trinaphthylporphyrin.

4-hydroxybenzaldehyde (3.053 g, 25 mmol), 1-Napthaldehyde (11.714 g, 75 mmol) and pyrrole (6.8 mL, 100 mmol) was added dropwise to 250 mL propionic acid in 20 min with stirring at 126 °C. The mixture was refluxed for 40 min, most of propionic acid was distilled away under reduced pressure and allowed to cool overnight. The black precipitate was filtered and washed with methane, and the crude product was purified by column chromatography ($CHCl_3$: methane, 50: 1, v: v) as eluent to collect the second fraction, bright purple crystalline 5-(4-hydroxyphenyl)-10,15,20-trinaphthylporphyrin (OH-TNP) was obtained (yield: 5.3%). Anal. Calcd for ($C_{56}H_{36}N_4O$): C 86.13, H 4.65, N 7.17. Found: C 86.23, H 4.67, N 7.13%. IR (KBr): v_{max} (cm^{-1}): 3432 (OH), 3316 (NH), 1608, 1505 (Ar), 1168 (Ar-O), 797 (Ar). ^{1}H NMR (500 MHz, $CDCl_3$, TMS), δ(ppm): 8.72-8.73 (d, 2H, J = 4.7 Hz, pyrrolic-β-CH), 8.51-8.54 (m, 2H, pyrrolic-β-CH), 8.41-8.43 (m, 4H, pyrrolic-β-CH), -2.39 (s, 2H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, TMS), δ(ppm): 155.33, 139.26, 139.23, 136.73, 135.59, 134.48, 132.80, 132.68, 132.61, 131.36, 131.31, 131.14, 131.09, 130.98, 128.55, 127.71, 126.09, 124.06, 117.54, 113.58. MALDI-TOF MS: calculated for ($C_{56}H_{36}N_4O$): *m/z* $[M + H]^+$ = 781.29; found: *m/z* = 782.2.

Synthesis of Poly(arylene ether ketone)s with carboxyl pendant.

Poly(arylene ether ketone)s with different molar ratio (0.1, 0.3, 0.5) of carboxyl pendant (PAEK-COOHs) were synthesized via copolymerization of 4,4'-difluorobenzophenone (DFB), 4,4'-(hexafluoroisopropylidene) diphenol and diphenolic acid as depicted in Scheme 1. A typical synthetic procedure (PAEK-COOH-30%) was carried out as follows: 4,4'-difluorobenzophenone (4.364 g, 20 mmol), 4,4'-(hexafluoroisopropylidene) diphenol (6FBPA) (4.707 g, 14 mmol), diphenolic acid (DPA) (1.717 g, 6 mmol), and anhydrous K_2CO_3 (3.455 g, 25 mmol) were dissolved in NMP (42 mL) and toluene (20 mL) in a three necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean-Stark trap with a condenser. The mixture was refluxed for 3 h at 130 °C under nitrogen to remove the resulting water. The reaction mixture was continued to react for 6 h at 160-170 °C to complete the polymerization. The viscous solution was poured into deionized water to precipitate the fibrous polymer, which was pulverized into powders, and washed thoroughly with boiling water and ethanol. The product was dissolved in 140 mL THF, 10 mL concentrated HCl was added dropwise to the solution with stirring, the reaction was continued at room temperature for 8 h, ensuring that the potassium carboxylate were completely converted to carboxyl groups. Then the polymer was precipitated in deionized water and washed, the product was dried to constant weight under vacuum at 100 °C for 24 h to give PAEK-COOH30%. Yield (92%). IR (KBr): v_{max} (cm^{-1}): 1732 (O=C-OH), 1658 (Ar-C=O), 1594, 1502 (Ar), 1264 (Ar-O-Ar).

The synthesis of PAEK-COOH10% and PAEK-COOH50% were conducted using the same procedure, but with the monomer feed ratios of 6FBPA : DPA being 90 : 10 and 50 : 50, respectively.

Synthesis of Poly(arylene ether ketone)s with porphyrin pendant.

A general procedure to synthesis the porphyrin grafted poly(arylene ether ketone)s was illustrated as Scheme 1 and conducted as follows: to a three-necked 100 mL flask fitted with a funnel drop, magnetic stirrer and nitrogen inlet were added 1.5 g (0.9 mmol of COOH) PAEK-COOH30%, 1.13 g (1.8 mmol) OH-TPP and 30 mL anhydrous THF. After the copolymer was dissolved, 20 mL anhydrous THF solution of 0.227 g (1.1 mmol) *N,N'*-dicyclohexylcarbodiimide (DCC) and 0.013 g (0.11 mmol) 4-(dimethylamino)pyridine (DMAP) was dropwise added in 2 h to avoid the formation of gel. The mixture was stirred at room temperature for 72 h under nitrogen, the solution was filtered to remove the white precipitate (dicyclohexylurea, DCU) and the purple filtrate was poured into ethanol to precipitate, then the polymer was dissolved/reprecipitate in THF/ethanol before extraction in acetone to remove the porphyrin residues. Finally, the product was dried under vacuum at 80 °C for 12 h, the purple polymer powders PAEK-COOH30%-TPP was prepared. IR (KBr): v_{max} (cm^{-1}): 3317 (NH), 1761 (O=C-O), 1658 (Ar-C=O), 1594, 1502 (Ar), 1264 (Ar-O-Ar), 799 (Ar).

Following the same procedure, a series of poly(arylene ether ketone)s with porphyrin pendants PAEK-COOH10%-TPP, PAEK-COOH50%-TPP, PAEK-COOH30%-TTP, and PAEK-COOH30%-TNP were synthesized with corresponding PAEK-COOH and feed ratios.

Metallization of Poly(arylene ether ketone)s with porphyrin pendant.

Poly(arylene ether ketone)s with zinc-porphyrin and lead-porphyrin pendant were synthesized using a similar method according to previous literature as illustrated in Scheme 2.[43] PAEK-COOH30%-TPP (1.00 g) was dissolved in *N,N'*-dimethylformamide (DMF) and stirred with excess $Zn(OAc)_2 \cdot 2H_2O$ (1.50 g) or $Pb(OAc)_2 \cdot 3H_2O$ (2.30 g) at 80 °C for 4 h, the product was precipitated into a large amount of ice water, washed with deionized water to remove unreacted acetate and isolated with filtration prior to being dried under vacuum to produce the final PAEK-COOH30%-ZnTPP (purple powders) and PAEK-COOH30%-PbTPP (green powders).

Results and discussion

Polymer Synthesis and Characterization

The poly(arylene ether ketone)s with porphyrin pendants were carried out by esterification of precursor copolymers (PAEK-COOH) using DCC and DMAP to activate carboxylic acid and mono-hydroxyphenyl porphyrins in anhydrous THF (Scheme 1). By immediately adding DCC into the PAEK-COOH solution, a gel was rapidly formed and could not be dissolved even under heating conditions as previously reported.44 This is because the carboxylic group of PAEK-COOH was prone to be converted to acid anhydride through intermolecular dehydration by the reaction of DCC in this system rather than intramolecular dehydration,45 resulting in crosslinking and the formation of gel, which prevented the nucleophilic DMAP from attacking the carbonyl group in the acid anhydride to form the intermediate. Therefore, this step was conducted by dropwise adding a THF solution of DCC and DMAP to control the reaction rate, thus the acid anhydride could react with DMAP to generate the intermediate. The viscosity of the polymer solution gradually increased with the addition of DCC at first and then decreased. Finally, the intermediate reacted with porphyrins to yield the target polymer and regenerate DMAP. After extraction in acetone for 48 h, the final product was examined by layer chromatography (TLC) to confirm the absence of residual porphyrins.

The molecular weights of the polymers were measured by GPC and displayed in Table 1, all the PAEKs were of high molecular weight. The molecular weights of PAEKs with porphyrin pendants are higher than those of the corresponding PAKE-COOH, indicating the successful grafting of porphyrins. However, PAEK-COOH30%-TNP has a lower Mn than PAEK-COOH30%-TPP and PAEK-COOH30%-TTP as a result of the bulkier OH-TNP, which further increased the steric hindrance and restricted the grafting degree. PAEK-COOH series were only soluble in polar solvents such as DMF and THF, after esterification, all the polymers with porphyrin pendants could be dissolved in chloroform, suggesting the improved solubility.

The structure of PAEKs with porphyrin pendants was confirmed by FTIR and 1H NMR spectroscopy. As shown in Fig. 1, the stretching vibration of the aromatic ketone C=O at 1658 cm-1, skeleton vibration of benzene rings at 1594 cm-1 and 1501 cm-1, and stretching vibration of ether linkage at 1246 cm-1 were observed for poly(arylene ether ketone)s. In comparison with the spectrum of PAEK-COOH30%, the absorption of carboxyl C=O at 1732 cm-1 disappeared, a new absorption band at 1761 cm-1 was detected in the spectra of polymers with porphyrins pendant, which was ascribed to the formation of ester bond. The existence of porphyrin moieties was confirmed by the weak characteristic absorption at 3317 cm-1 and 799 cm-1, corresponding to the internal –NH and porphyrin ring, respectively. However, after complexation with Zn2+ or Pb2+ the absorption band of –NH in porphyrin moieties disappeared, indicating the complete metallization. It should be noted that in the spectra of PAEK-COOH30%-TTP and PAEK-COOH30%-TNP (Fig. S1), the absorption of residual carboxyl C=O at 1710 cm-1 could be found compared with the spectra of analogous PAEK-COOH30%-TPP, despite of their identical reaction process. These results are consistent with the GPC results of PAEK-COOH30%-TNP, which implied a lower grafting degree.

Fig. 2 shows the 1H NMR spectra of the PAEK-COOH30% and PAEKs with three porphyrin pendants based on PAEK-COOH30%. The aromatic region of the polymers exhibited signals at 7.86, 7.43, and 7.25 ppm corresponding to protons a, c, and e, the integral ratio was calculated to coincide with the initial stoichiometric proportion. Signals from 7.03 to 7.12 ppm were assigned to protons around the ether linkage b and d, while the signals from 2.03 to 2.45 ppm were assigned to protons of aliphatic –CH2– and –CH3. Whereas for polymers with porphyrin pendants, the signals attributable to porphyrin moieties from 7.13 to 8.86 could be observed, which slightly shifted relative to those of OH-TPP (see Fig. S2). In addition, the characteristic singlet of internal pyrrole –NH proton at –2.76 ppm appeared in PAEK-COOH30%-TPP, and disappeared after the complexation with Zn2+ and Pb2+ as expected (see Fig. S3).

To further corroborate the presence and distribution of metal elements in a polymer matrix, Energy dispersive spectrometry (EDS) was employed as it provides direct information regarding the contents of the target elements. The mass fractions (wt%) of Zn and Pb on the selected area of polymer film surface were found to be 2.3% and 6.95%, from which the wt% of porphyrin were calculated to be 22.1% and 21.1%. The EDS mapping photographs of PAEK-COOH30%-ZnTPP and PAEK-COOH30%-PbTPP films were shown in Fig. S4 at magnifications of 800 k. The well-dispersed red/green dots represented the position of Zn/Pb element, indicating that porphyrins were densely and uniformly distributed in the matrix, the agglomeration or phase separation was not observed in the film samples, despite of the extremely high porphyrin content.

The wide-angle X-ray diffraction profiles of the neat PAEK-COOH30% film (Fig. 3) exhibited a typical pattern of amorphous polymers centered at 2θ = 16.3° and a shoulder at 2θ = 6.4°, the solid state pure OH-TPP sample displayed multiple sharp diffraction peaks, suggesting a crystalline structure. The position of the maximum for PAEK-COOH30%-TPP and PAEK-COOH50%-TPP shifted to a higher position at 2θ = 17.8°, a shoulder was also observed at 2θ = 7.3°. The diffuse peaks of the resultant PAEKs with porphyrin pendants manifested the good compatibility of porphyrins with the poly(arylene ether ketone)s, and the agglomeration of porphyrins was precluded due to covalent linkage. Moreover, it is favorable to fabricate optical films since the incorporation of porphyrins in the sidechains retained the amorphous nature of the polymer.

Thermal Stabilities and Mechanical Properties

The thermal properties of these polymers were evaluated by DSC and TGA in a nitrogen atmosphere as shown in Table 2, it can be seen that all polymers with porphyrin pendants possessed higher glass transition temperatures (T_g) than their precursor polymers PAEK-COOH. Generally, the conversion from polar groups to nonpolar groups in polymers results in a decrease in T_g due to the reduced intermolecular force. On the other hand, the presence of bulky pendant substituents would confine the segmental motion, leading to an increase of T_g. In this work, the bulkiness of porphyrin pendants seemed to play a more important role, and the T_g markedly increased as the porphyrin pendants content increased (Fig. 4a) It should be noted that metallization further elevated the T_g value of PAEK-30%COOH-TPP by 10 ^oC approximately, similar situation has been reported in polyimides containing metalporphyrins, where the incorporation of Zn^{2+} enhanced the rigidity of the planar macrocyclic structure, thus impeded the segmental motion at the same porphyrin content.[46] Thermal stability is vital to optical limiting materials due to the thermal effect induced by laser. As illustrated in Fig. 5a, the TGA curves of the polymers exhibited two degradation step. The first weight loss at about 140 ^oC was associated with the degradation of carboxyl or ester group, the PAEKs with porphyrin pendants showed slightly more initial weight loss when compared with their corresponding starting polymers PAEK-COOH, indicating the weaker thermal stability of ester linkage. Fig. 5b shows the TGA curves of poly(arylene ether ketone)s with different porphyrin pendants based on PAEK-COOH30%. For the metalporphyrin counterparts, no significant distinction was detected in the weight loss curves but a higher char yield due to the presence of central metal. By contrast, PAEK-COOH30%-TTP showed a much poorer thermal stability, which might be attributed to the structure of tritolyporphyrin. The 5% and 10% decomposition temperatures of the polymers are presented in Table 2, the conclusion can be drawn that the incorporation of porphyrins slightly decreased the thermal stabilities of the starting copolymers, this phenomenon was in agreement with other polymers wearing ester pendant groups.[44]

The mechanical properties of the PAEK films cast from THF are summarized in Table 2. The PAEKs with carboxyl group possessed Young's modulus from 2.03 to 2.14 GPa, tensile strength from 67.4 to 72.4 MPa, and elongation at break from 12.7% to 24.1%. When the carboxyl groups were converted into porphyrin pendants via esterification, their Young's modulus and tensile strength decreased to some extent, one of the major reasons was that the polar PAEK-COOHs had a stronger intermolecular force. The elongation at break of the polymers decreased as well after esterification, on one hand, the incorporation of rigid macrocyclic group in to the polymer matrix usually brought about brittleness.[47] On the other hand, as mentioned above, DCC/DMAP catalyzed esterification was likely to result in a slight crosslinking structure in the current system that decreased the elongation at break. From these results, it can be stated that, the prepared poly(arylene ether ketone)s with porphyrin pendants retained good thermal stabilities and mechanical properties of high performance polymers, and showed the application prospect as a new species of NLO material.

Photophysical Properties

The ground state absorption of the highly delocalized aromatic porphyrins is mostly confined to a few narrow regions, an intense *Soret* band ascribed to $\pi\rightarrow\pi^*$ transitions and several *Q* bands from 500 nm to 700 nm, which can be modulated by the central metal, the type of axial ligands, or the nature of the peripheral substituents as previously reported.[9-12] UV-vis spectroscopy of the prepared polymers in chloroform was employed to monitor the variation of their linear optical properties. As shown in Fig. 6, all polymer solutions showed absorption before 300 nm due to the electron transitions of aromatic ketones in the backbone, but no absorption was detected in PAEK-COOH30% in the visible region. PAEKs with TPP, TTP, and TNP pendants exhibited intense *Soret* bands at 418, 420, and 422 nm (attributed to S_0-S_2 transition), respectively. In the case of PAEKs with Zn-TPP and Pb-TPP pendants, the *Soret* band shifted to 423 and 466 nm. It is known that the complexation with metal ions result in a distinct shift in *Soret* band and a reduction of *Q* bands due to the configuration interaction, the *Q* bands absorption of our polymers is consistent with this nature (Fig. S5). PAEK-COOH30%-TPP exhibited four weak *Q* bands at 515, 550, 590, and 648 nm, whereas for PAEK-COOH30%-ZnTPP and PAEK-COOH30%-PbTPP the *Q* bands reduced to two with a red shift.

Fluorescence measurements were performed on the polymers at a low concentration (maximum absorption less than 0.05) to avoid self-quenching. The emission spectra are given in Fig. 7, PAEKs with TPP, TTP, and TNP pendants showed a similar emission band in the red region at 650-710 nm attributed to the porphyrin moieties. TTP and TNP pendants showed a minor red shift due to the presence of electron-donating group and the enlarged conjugation. PAEK with ZnTPP exhibited emission band at 600 and 649 nm, whereas the incorporation of Pb^{2+} completely quenched the fluorescence of porphyrin due to the heavy-atom effect, thus increased the efficiency in intersystem crossing from S_1 to T_1. The relative fluorescence quantum yields were determined by previously reported method, where a freshly prepared free base tetraphenylporphyrin (TPP) in air-saturated benzene was used as a standard.[48] As shown in Table 1, all polymers were excited at their maximum excitation wavelength, the quantum yields of the PAEKs were similar with that of TPP in benzene (0.11), this observation demonstrated that no substantial electron interaction from porphyrins to the polymer backbone occurred via ester linkage. Among the poly(arylene ether ketone)s with porphyrin pendants, PAEK-COOH30%-TTP exhibited the highest quantum yield of 0.13.

Nonlinear Optical and Optical Limiting Properties

The nonlinear optical behavior of the polymers in THF were measured by using *Z*-scan technique under open-aperture and closed-aperture configuration with 4 ns pulsed laser irradiation at 532 nm with an intensity of 5.3 μJ. To investigate the effect of the porphyrin pendants on the NLO properties, Open *Z*-scan experiments of PAEKs with porphyrins of different contents, peripheral substituents, and central metal in THF were performed by comparison. As shown in Fig. 8, the normalized transmittance curves showed a symmetrical peak with respect to the focus, indicating that the attachment of porphyrin moieties endowed PAEKs nonlinear absorption, as the samples exhibited a decreased transmittance when they were brought closer to focus. The linear transmittance of PAEK-COOH10%-TPP, PAEK-COOH30%-TPP, and PAEK-COOH50%-TPP were determined to be 83%, 65%, and 56% at the same concentration of 0.25 mg/mL, respectively. The NLO properties in the ns region can be described using a five-level model RSA process: the ground state (S_0) of a molecule is excited to the first singlet state (S_1) by a laser pulse, after that several competing process occurs, such as radiationless relaxation, fluorescence, and intersystem crossing (ISC) from S_1 to triplet state (T_1) with a time constant (τ_{ISC}) of nanoseconds. The latter has a large excited state absorption cross section (σ_{ex}), thus gives a strong nonlinear absorption to the incident laser beam.[9,10,49] The RSA curve of PAEK-COOH50%-TPP showed the deepest valley due to the largest porphyrin amount at the expense of the lowest linear transmittance. While there was no NLO signal observed in the THF solution of PAEK-COOH30%, which had a linear transmittance of 91%.

Fig. 9 represented the open *Z*-scan curves of PAEKs with various porphyrin pendants based on PAEK-COOH30%. To evaluate their NLO response by comparison, all samples were adjusted to have the same linear transmittance of 65%. It was observed that PAEKs with TPP and TTP pendants showed similar profiles with the normalized nonlinear transmittance of 0.69 at the focus, the β values were determined to be 7.61×10^{-10} and 7.5×10^{-10} m W^{-1} from theoretical fitting. Whereas for PAEK-COOH30%-TNP, the transmittance decreased to 0.61 with β of 1.21×10^{-9} m W^{-1}, indicating a stronger NLO response due to an extended conjugated system at the same level of incident energy. When the metal ions Zn^{2+} and Pb^{2+} were inserted to PAEK-COOH30%-TPP, the nonlinear absorption coefficient β significantly increased by one order of magnitude, and the transmittance decreased to 0.6 and 0.4. It is well known that the electrical configuration of the central ions plays an important role on ISC and relaxation time, involving spin-orbit coupling through Coulombic exchange terms. Zn^{2+} and Pb^{2+} have closed shells, which result in high ISC rates, high yields and long lifetime of triplet excited states, thus giving rise to the enhanced RSA.[9-11] PAEK-COOH30%-PbTPP exhibited the largest NLO response of all the samples with β of 3.9×10^{-9} m W^{-1}, the fitting obtained from the data of PAEK-COOH30%-PbTPP is not perfect, this may be induced by the change of beam at high pulse energy. These results were two orders of magnitude larger than those of our previous work, where the NLO properties of PAEKs incorporating porphyrins in the backbones were investigated by 21 ps pulsed laser system.[50] The much larger β values in the present work were primarily attributed to the longer laser pulse relative to τ_{ISC} that allowed the transformation from S_1 to T_1.

In addition, closed-aperture *Z*-scan measurements demonstrated the nonlinear refraction response in THF of PAEKs with porphyrin pendants, which was not observed in those of PAEKs with metal porphyrin pendants (Fig. S6). The curves (peak-valley) indicated that the nonlinear refraction of PAEK-COOH30%-TPP resulted from the thermally induced self-defocusing effect, suggesting a negative nonlinear refraction coefficient (Table 3).

The optical limiting performances of the polymer were measured in THF with the same laser system, the normalized transmittance or output fluence was plotted as functions of input fluence (J cm^{-2}). The OL behavior of PAEK-COOH10%-TPP, PAEK-COOH30%-TPP, and PAEK-COOH50%-TPP were shown in Fig. S7 at the same concentration. It can be observed that at low incident energy, the output increased linearly with the input fluence obeying Beer's Law, as the incident energy increased, the output fluence significantly deviated from linearity. PAEK-COOH50%-TPP showed the best OL performance due to the largest porphyrin amount per unit volume, which was consistent with their open *Z*-scan curve. The curves of normalized transmittance versus input fluence for PAEKs bearing various porphyrin pendants based on PAEK-COOH30% were gathered in Fig. 10, all the samples were adjusted to have the same linear transmittance at 532 nm in THF. The results are in agreement with the nonlinear absorption derived from *Z*-scan measurements, following a similar trend that PAEK-COOH30%-PbTPP showed the best OL performance with the limiting threshold (incident fluence at which the transmittance falls to 50% of the linear transmittance) of 0.3 J/cm^2. Generally, the OL property can be evaluated by the ratio of excited state absorption cross section (σ_{ex}) to the ground state absorption cross section (σ_0) $\sigma_{ex}/\sigma_0 = \ln T_{sat}/\ln T_0$, T_{sat} is the saturated transmittance for high degrees of excitation. Although the saturated transmittance is unable to reach in our experiment setup, we can use the method in some reports, [51] where the transmittance at maximum input fluence (1.4 J/cm^2) is employed to calculate the lowest bound for σ_{ex}/σ_0, and the values are 1.8, 2.0, 2.4, 2.6, and 3.7 for the THF solution of PAEK with TPP, TTP, TNP, ZnTPP, and PbTPP pendants, respectively.

The application of porphyrins in a practical optical limiting device would inevitably require the homogeneous incorporation in the solid state. Based on this consideration, we prepared thin films of PAEK-COOH30%-TPP, PAEK-COOH30%-ZnTPP, and PAEK-COOH30%-PbTPP using conventional spin-coating on quartz glass substrates (diameter: 37 mm, thickness: 2mm) to preliminarily evaluate their OL performance. Their linear transmittance were measured to be 55%, 68%, and 73%, respectively. Form Fig. 11, it can be observed that the transmittance of PAEKs with porphyrin pendants started to decrease before 50 mJ/cm^2, indicating remarkable OL effect. It is worth mentioning that the polymers showed improved OL performance in films than those in THF, the limiting threshold was found to be 0.3 J/cm^2 for PAEK-COOH30%-PbTPP, and the THF solutions of PAEK-COOH30%-TPP and PAEK-COOH30%-ZnTPP were unable to attenuate the incident energy to a threshold. Whereas for film samples, their limiting threshold were determined to be 0.29, 0.30, and 0.15 J/cm^2 for PAEK-COOH30%-TPP, PAEK-COOH30%-ZnTPP, and PAEK-COOH30%-PbTPP, respectively. Hence, according to the results, the PAEKs with porphyrin pendants possessed good performance as optical limiting materials in both solution and in solid state.

Conclusions

A series of novel poly(arylene ether ketone)s with porphyrin pendants of different structure were synthesized via an esterification reaction using DCC and DMAP to activate the carboxyl groups. The porphyrin pendant moieties endowed PAEKs with strong fluorescent intensity, excellent solubility (particularly in $CHCl_3$), much higher T_g values, and lower decomposition temperatures compared with the starting copolymers. More importantly, the combination of porphyrin chromophores with poly(arylene ether ketone)s retained the excellent nonlinear optical properties and the good film formability of each component, as demonstrated by *Z*-scan technique and optical limiting measurements. Poly(arylene ether ketone) with PbTPP pendants showed the largest nonlinear optical coefficient β of 3.9×10^{-9} m W^{-1} and the lowest limiting threshold of 0.3 J/cm^2 in THF. In addition, it was found the polymers in homogeneous thin film state exhibited enhanced OL performance, which provides a new facile synthetic approach for designing high performance polymer based optical limiter.

Acknowledgements

This research was financially supported by the PhD Program Foundation of the Ministry of Education of China (No. 20120061110017) and Changchun Science and Technology Development Plan Program of China (2013050). We also acknowledge the support from Prof. Yinglin Song of Soochow University for the *Z*-scan and optical limiting measurements.

Notes and references

[a]College of Chemistry, Key Laboratory of High Performance Plastics, Ministry of Education, Jilin University, Changchun 130012, China

[b]College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, China

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

(1) L. W. Tutt and A. Kost, *Nature*, 1992, **356**, 225-226.
(2) D. M. Burland, R. D. Miller and C. Walsh, *Chem. Rev.*, 1994, **94**, 31-75.
(3) G. I. Stegeman, D. J. Hagan and L. Torner, *Opt. Quant. Electron.*, 1996, **28**, 1691-1740.
(4) C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013-2020.
(5) T. J. Mckay, J. Staromlynska, P. Wilson and J. Davy, *J. Appl. Phys.*, 1999, **85**, 1337-1341.
(6) G. J. Zhou and W. Y. Wong, *Chem. Soc. Rev.*, 2011, **40**, 2541-2566.
(7) L. W. Tutt and T. F. Boggess, *Prog. Quantum. Electron.*, 1993, **17**, 299-338.
(8) D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelick, P. A. Fleitz and T. Pottenger, *Opt. Lett.*, 1993, **18**, 858-860.
(9) M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos and E. M. N. Mhuircheartaigh, *Adv. Mater.*, 2007, **19**, 2737-2774.
(10)M. Calvete, G. Y. Yang and M. Hanack, *Syn. Met.*, 2004, **141**, 231-243.
(11)W. Blau, H. Byrne, W. M. Dennis and J. M. Kelly, *Opt. Commun.*, 1985, **56**, 25-29.
(12)A. K. Harry, H. L. Anderson, G. B. Ross, S. Clark and K. J. McEwan, *Adv. Mater.*, 2001, **13**, 652-656.
(13)J. C. Feng, Q. H. Zhang, W. Li, Y. Li, M. J. Yang and Y. Cao, *J. Appl. Polym. Sci.*, 2008, **109**, 2283-2290.
(14)K. T. Nielsen, H. Spanggaard and F. C. Krebs, *Macromolecules*, 2005, **38**, 1180-1189.
(15)L. S. Wan, J. Wu and Z. K. Xu, *Macromol. Rapid. Commun.*, 2006, **27**, 1533-1538.
(16)Y. Y. Lv, J. Wu, L. S. Wan and J. K. Xu, *J. Phys. Chem. C.*, 2008, **112**, 10609-10615.
(17)T. E. O. Screen, K. B. Lawton, G. S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson, S. J. Martin, D. D. C. Bradley and H. L. Anderson, *J. Mater. Chem.*, 2001, **11**, 312-320.
(18)X. B. Huang, Q. Q. Shi, W. Q. Chen, C. L. Zhu, W. Y. Zhou, Z. Zhao, X. M. Duan and X. W. Zhang, *Macromolecules*, 2010, **43**, 9620-9636.
(19)R. A. Schmitz, P. A. Liddell, G. Kodis, M. J. Kenney, B. J. Brennan, N. V. Oster, T. A. Moore and D. Gust, *Phys. Chem. Chem. Phys.*, 2014, **16**, 17569-17579.
(20)V. S. P. K. Neti, X. F. Wu, S. G. Deng and L. Echegoyen, *Polym. Chem.*, 2013, **4**, 4566-4569.
(21)L. J. Feng, Q. Chen, J. H. Zhu, D. P. Liu, Y. C. Zhao and B. H. Han, *Polym. Chem.*, 2014, **5**, 3081-3088.
(22)A. L. Wirotius, E. Ibraboure, L. Scarpantonio, M. Schappacher, N. D. McClenaghan and A. Deffieux, *Polym. Chem.*, 2013, **4**, 1903-1912.
(23)T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, *Polymer*, 1981, **22**, 1096-1103.
(24)P. M. Hergenrother, B. J. Jensen and S. J. Havens, *Polymer*, 1988, **29**, 358-369.
(25)J. B. Rose, *Polymer*, 1974, **15**, 456-465.
(26)A. Jonas and R. Legras, *Polymer*, 1991, **32**, 2691-2706.
(27)M. G. Dhara and S. Banerjee, *Prog. Polym. Sci.*, 2010, **35**, 1022-1077.
(28)B. J. Liu, G. B. Wang, W. Hu, Y. H. Jin, C. H. Chen, Z. H. Jiang, W. J. Zhang, Z. W. Wu and Y. Wei, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 3392-3398.
(29)J. F. Ding, F. T. Liu and M. Li, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 4205-4216.
(30)B. J. Liu, W. Hu and G. P. Robertson, *J. Mater. Chem.*, 2008, **18**, 4675-4682.
(31)W. J. Cantwell and J. Morton, *Composites*, 1991, **22**, 347-362.
(32)K. Friedrich, R. Walter, H. Voss and J. Karger-Kocsis, *Composites*, 1986, **17**, 205-216.
(33)B. J. Liu, G. P. Robertson, D. S. Kim, M. D. Guiver, W. Hu and Z. H. Jiang, *Macromolecules*, 2007, **40**, 1934-1944.
(34)B. Bae, T. Yoda, K. Miyatake, H. Uchida and M. Watanabe, *Angew. Chem., Int. Ed.*, 2010, **122**, 327-330.
(35)S. Gu, R. Cai and Y. Yan, *Chem. Commun.*, 2011, **47**, 2856–2858.
(36)Z. Zhao, J. Wang, S. Li, and S. Zhang, *J. Power Sources*, 2011, **196**, 4445-4450.
(37)D. Y. Chen, M. A. Hickner *Macromolecules*, 2013, **46**, 9270-9278.
(38)G. Maier, *Prog. Polym. Sci.*, 2001, **26**, 3-65.
(39)Z. Geng, M. X. Huo, J. X. Mu, S. L. Zhang, Y. N. Lu, J. S. Luan, P. F. Huo, Y. L. Du and G. B. Wang, *J. Mater. Chem. C*, 2014, **2**, 1094-1103.
(40)R. Westlund, E. Malmstrom, C. Lopes, J. Ohgren, T. Rodgers, Y. Saito, S. Kawata, E. Glimsdal and M. Lindgren, *Adv. Funct. Mater.*, 2008, **18**, 1939-1948.
(41)C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013-2020.
(42)A. D. Alder, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korakoff, *J. Org. Chem.*, 1967, **32**, 476-476.
(43)L. J. Twyman, A. Ellis and P. J. Gittins, *Macromolecules*, 2011, **44**, 6365-6369.

(44)E. M. Maya, I. Garcia-Yoldi, A. E. Lozano, J. G. de la Campa and J. de Abajo, *Macromolecules*, 2011, **44**, 2780-2790.

(45)Y. L. Luo, Q. P. Ran, S. S. Wu and J. Shen, *J. Appl. Polym. Sci.*, 2008, **109**, 3286-3291.

(46)W. Anannarukan,; S. Tantayanon, D. Zhang, E. A. Aleman, D. A. Modarelli and F. W. Harris, *Polymer*, 2006, **47**, 4936-4945.

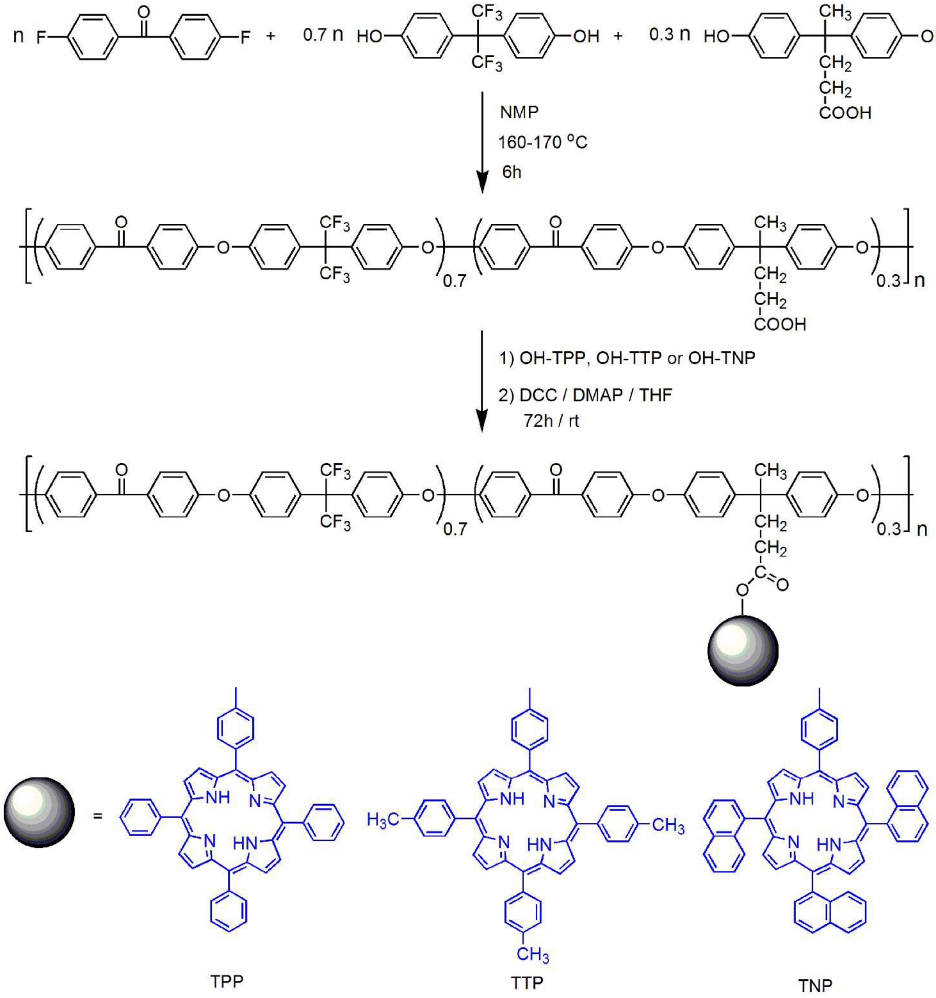
(47)L. J. Gao, F. G. Du, M. Xiao, S. J. Wang and Y. Z. Meng, *J. Appl. Polym. Sci.*, 2008, **108**, 3626-3631.

(48)D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, 1975, **97**, 5111-5117.

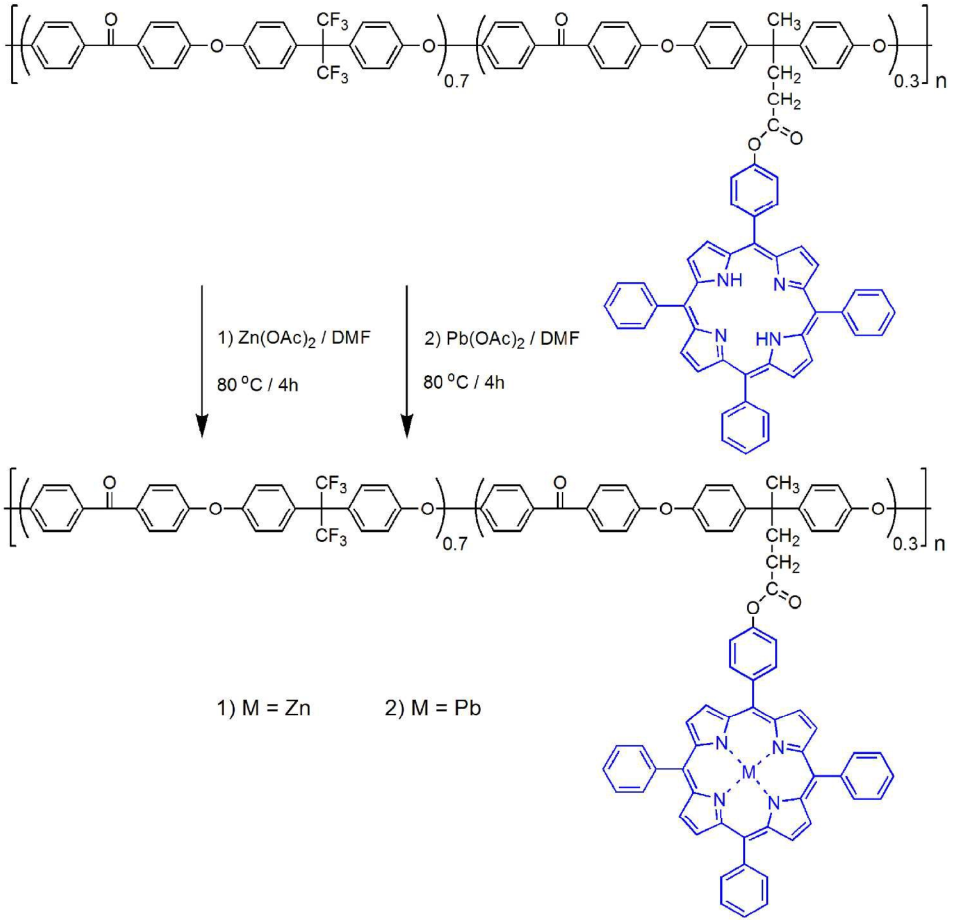
(49)Y. Chen, M. Hanack, Y. Araki and O. Ito, *Chem. Soc. Rev.*, 2005, **34**, 517-529.

(50)Y. L. Du, S. L. Zhang, X. Jiang, K. Zhu, Z. Geng, Y. Fang, P. F. Huo, C. Liu, Y. L. Song and G. B. Wang, *J. Polym. Sci. Part A: Polym. Chem.*, 2014, **52**, 1282-1290.

(51)X. Y. Su, S. Y. Guang, C. W. Li, H. Y. Xu, X. Y. Liu, X. Wang and Y. L. Song, *Macromolecules*, 2010, **43**, 2840-2845.



Scheme 1. Synthesis of PAEKs with porphyrin pendants.



Scheme 2. Synthesis of PAEK-COOH30%-ZnTPP and PAEK-COOH30%-PbTPP.

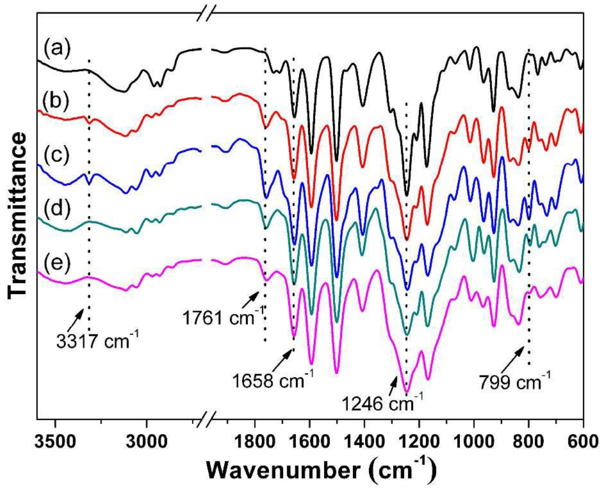


Fig. 1 IR spectra of (a) PAEK-COOH30%, (b) PAEK-COOH30%-TPP, (c) PAEK-COOH50%-TPP, (d) PAEK-COOH30%-ZnTPP, and (e) PAEK-COOH30%-PbTPP.

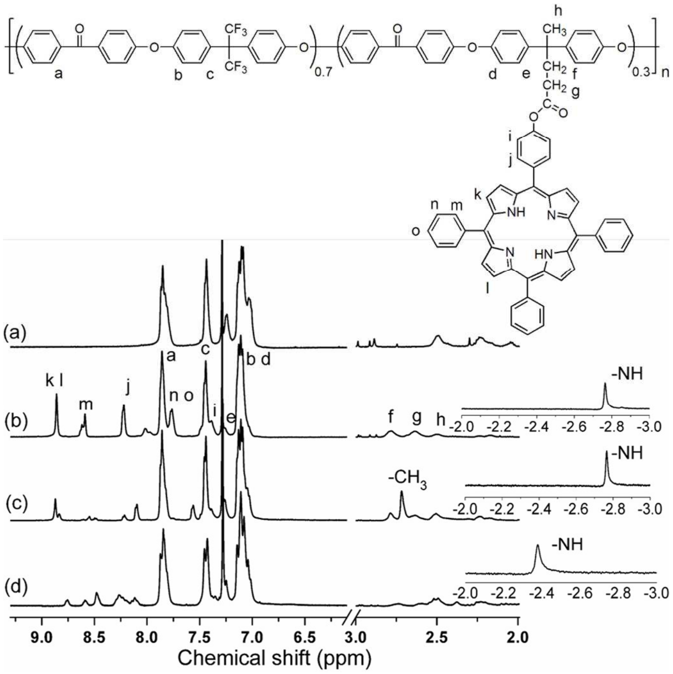


Fig. 2 ^{1}H NMR spectra of (a) PAEK-COOH30%, (b) PAEK-COOH30%-TPP, (c) PAEK-COOH30%-TTP, (d) PAEK-COOH30%-TNP.

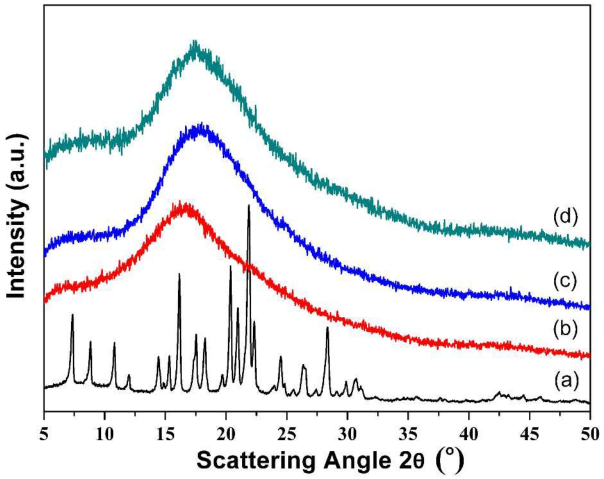


Fig. 3 WAXD profiles of (a) pure OH-TPP, (b) PAEK-COOH30%, (c) PAEK-COOH30%-TPP, (d) PAEK-COOH50%-TPP.

Journal Name RSCPublishing

ARTICLE

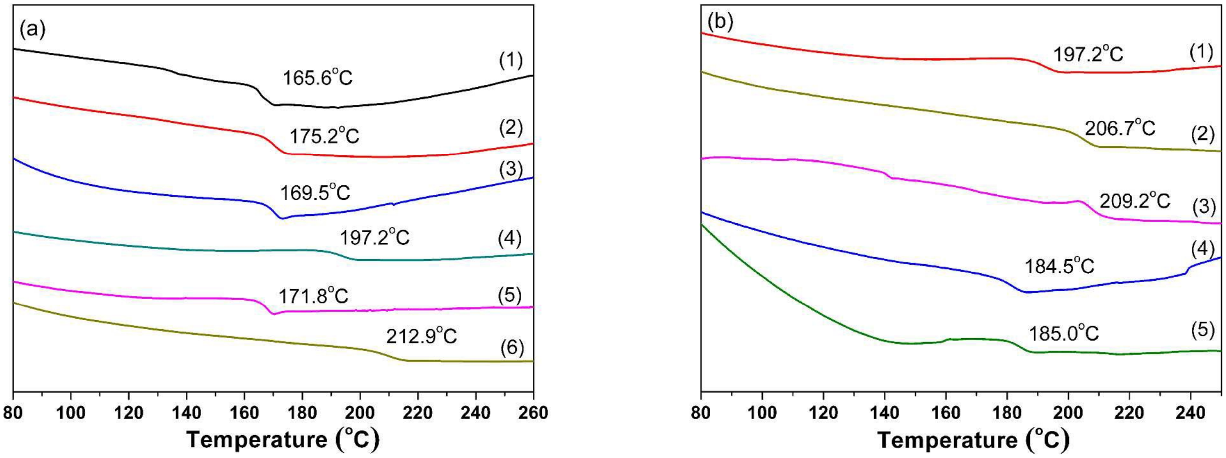


Fig. 4 (a) DSC curves of (1) PAEK-COOH10%, (2) PAEK-COOH10%-TPP, (3) PAEK-COOH30%, (4) PAEK-COOH30%-TPP, (5) PAEK-COOH50%, and (6) PAEK-COOH50%-TPP. (b) DSC curves of (1) PAEK-COOH30%-TPP, (2) PAEK-COOH30%-ZnTPP, (3) PAEK-COOH30%-PbTPP, (4) PAEK-COOH30%-TTP, and (5) PAEK-COOH30%-TNP.

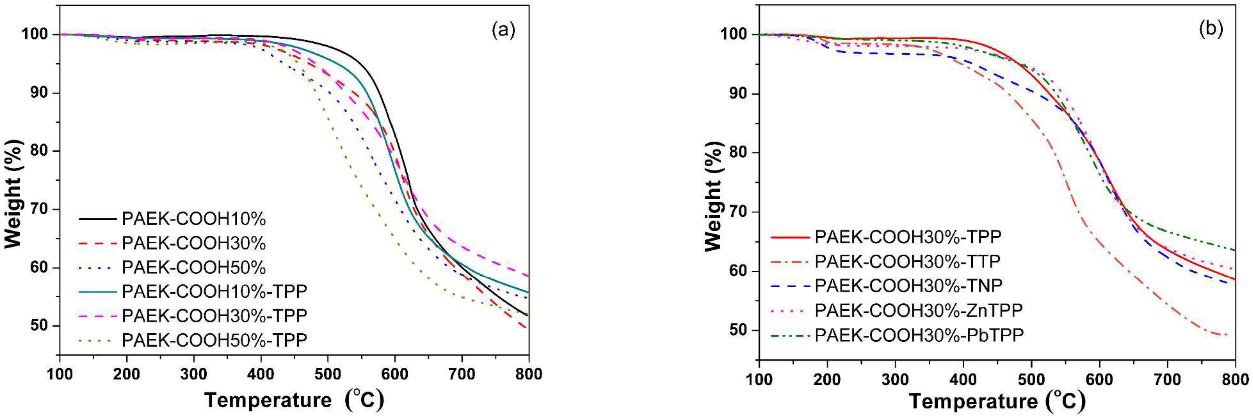


Fig. 5 (a) TGA analysis of PAEKs with different contents of porphyrin pendants. (b) TGA analysis of PAEKs with various porphyrin pendants based on PAEK-COOH30%.

‘

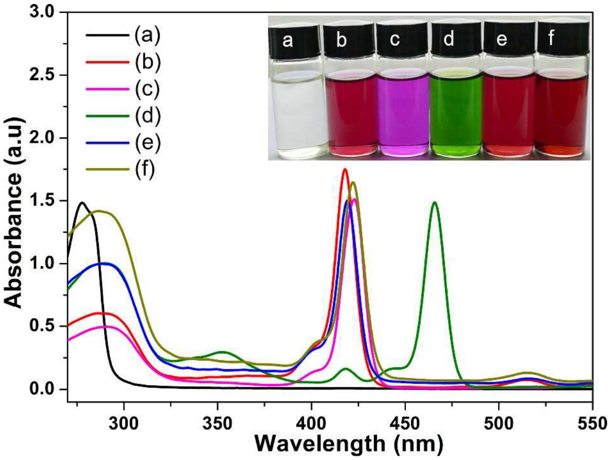


Fig. 6 UV-vis absorption spectra of (a) PAEK-COOH30%, (b) PAEK-COOH30%-TPP, (c) PAEK-COOH30%-ZnTPP, (d) PAEK-COOH30%-PbTPP, (e) PAEK-COOH30%-TTP, and (f) PAEK-COOH30%-TNP.

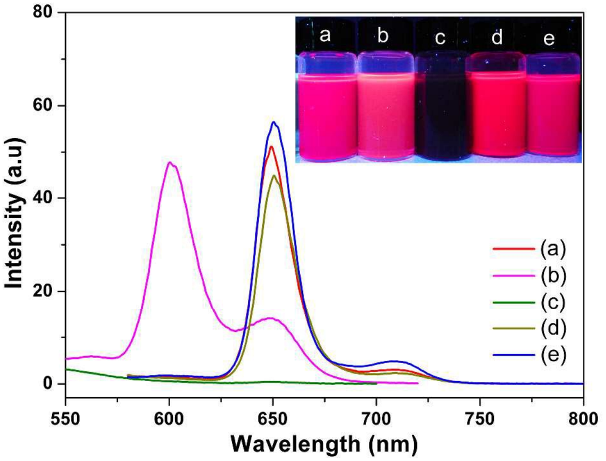


Fig. 7 Fluorescence emission spectra of (a) PAEK-COOH30%-TPP, (b) PAEK-COOH30%-ZnTPP, (c) PAEK-COOH30%-PbTPP, (d) PAEK-COOH30%-TTP, and (e) PAEK-COOH30%-TNP. Inset: photographs of polymer solution under a hand-held UV-lamp with λ_{max} = 365 nm.

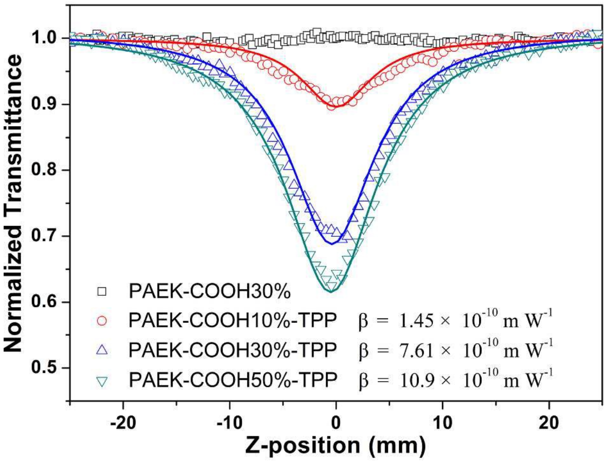


Fig. 8 Normalized Open-*Z* scan curves of PAEK-COOH30%, PAEK-COOH10%-TPP, PAEK-COOH30%-TPP, and PAEK-COOH50%-TPP at a concentration of 0.25 mg/mL at 532 nm. Solid lines represents theoretical fits.

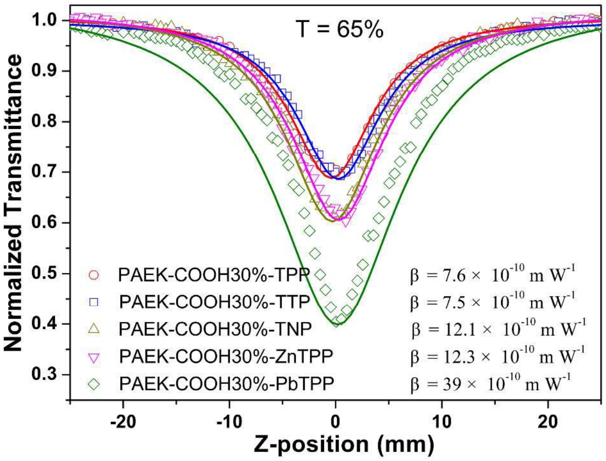


Fig. 9 Open-*Z* scan curves of PAEKs with various porphyrin pendants based on PAEK-COOH30% at the linear transmittance of 65%. Solid lines represents theoretical fits.

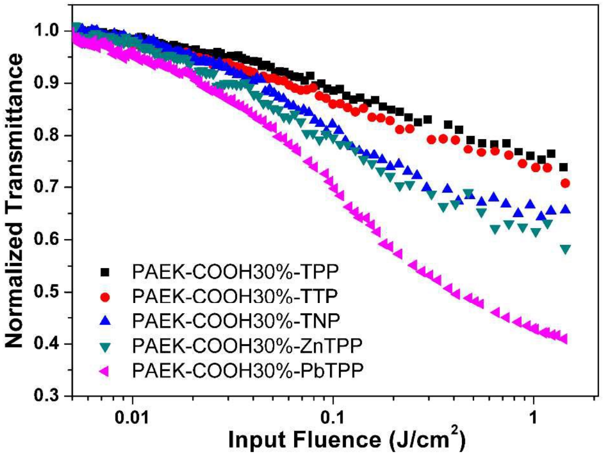


Fig. 10 Optical limiting responses of PAEKs with various porphyrin pendants based on PAEK-COOH30% in THF.

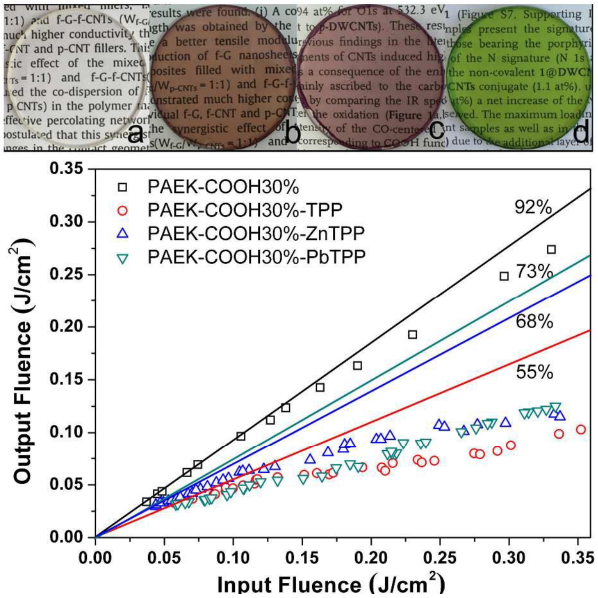


Fig. 11 Photographs of (a) PAEK-COOH30%, (b) PAEK-COOH30%-TPP, (c) PAEK-COOH30%-ZnTPP, and (d) PAEK-COOH30%-PbTPP films prepared by spin-coating and their OL responses.

Table 1. Molecular Weight and Optical Properties of poly(arylene ether ketone)s

Polymer	M_n (kg/mol)^a	M_w (kg/mol)^a	PDI^a	*Soret* Band (nm)	Emission Bands (nm)^b	$\Phi_F{}^c$
PAEK-COOH10%	53.5	95.0	1.78			
PAEK-COOH30%	57.4	95.7	1.67			
PAEK-COOH50%	39.4	79.8	2.03			
PAEK-COOH10%-TPP	68.9	129.5	1.88	418	651,708	0.087
PAEK-COOH30%-TPP	75.9	151.8	2.00	418	649,708	0.091
PAEK-COOH50%-TPP	68.6	107.7	1.57	418	649,708	0.101
PAEK-COOH30%-ZnTPP	83.2	144.8	1.74	423	600,649	0.089
PAEK-COOH30%-PbTPP	78.3	150.3	1.92	466		
PAEK-COOH30%-TTP	62.4	138.6	2.22	420	651,709	0.131
PAEK-COOH30%-TNP	61.8	107.8	1.74	422	652,707	0.103

a Evaluated by GPC eluted with THF, using polystyrene as a standard.

b Excited at the maximum excitation wavelength.

c Determined using free base TPP in benzene (ΦF = 0.11) as a standard according to the report[47].

Table 2. Thermal and Mechanical of Poly(arylene ether ketone)s Films

Polymer	T_g^a (°C)	T_{d5} (°C)	T_{d10} (°C)	Tensile modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)
PAEK-COOH10%	165.6	547.8	576.6	2.03	67.4	24.1
PAEK-COOH30%	169.5	472.8	539.4	2.11	67.8	19.3
PAEK-COOH50%	171.8	434.4	502.5	2.14	72.4	12.7
PAEK-COOH10%-TPP	175.2	514.2	557.9	2.09	64.2	7.2
PAEK-COOH30%-TPP	197.2	481.2	526.6	1.82	60.6	8.7
PAEK-COOH50%-TPP	212.9	455.4	482.1	1.84	61.2	8.0
PAEK-COOH30%-ZnTPP	206.7	488.6	546.1	2.01	64.2	7.5
PAEK-COOH30%-PbTPP	209.2	484.0	536.4	1.88	62.5	8.3
PAEK-COOH30%-TTP	185.0	397.9	466.6	2.03	63.3	6.4
PAEK-COOH30%-TNP	184.5	415.7	508.5	1.97	63.8	5.8

[a] From the second heading trace of DSC measurements conducted at a heating rate of 20 °C min^{-1}

Table 3. Nonlinear Optical Properties of poly(arylene ether ketone)s with porphyrin pendants

Polymer	Transmittance	Nonlinear optical values[a]			
		β (m W^{-1})	n_2 (m^{-2} W)	$\lvert\chi^{(3)}\rvert$ (esu)	σ_{ex}/σ_0[b]
PAEK-COOH10%-TPP	83%	1.45×10^{-10}	-1.5×10^{-17}	3.56×10^{-11}	1.6
PAEK-COOH30%-TPP	65%	7.61×10^{-10}	-4.5×10^{-17}	1.09×10^{-10}	1.8
PAEK-COOH50%-TPP	56%	10.9×10^{-10}	-3.5×10^{-17}	8.52×10^{-11}	1.8
PAEK-COOH30%-ZnTPP	65%	12.3×10^{-10}		3.91×10^{-11}	2.6
PAEK-COOH30%-PbTPP	65%	39×10^{-10}		1.24×10^{-10}	3.7
PAEK-COOH30%-TTP	65%	7.5×10^{-10}	-3.5×10^{-17}	8.14×10^{-11}	2.0
PAEK-COOH30%-TNP	65%	12.1×10^{-10}	-6.5×10^{-17}	1.58×10^{-10}	2.4

[a] Measured by *Z*-scan technique with 4 ns Nd:YAG laser system at 10 Hz and 532 nm, the values were determined by fitting the experimental data.

[b] calculated by ln T_{sat}/ln T_0, where T_{sat} is replaced by the transmittance at 1.4 J/cm^2.