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Poly(arylene ether)s with aromatic azo-coupled cobalt phthalocyanines in the side chain: synthesis, characterization and nonlinear optical and optical limiting properties

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A novel poly(arylene ether) with azo-coupled cobalt phthalocyanine in the side chain (PAE-azo-CoPc) was prepared by 1,2-benzodinitrile, anhydrous cobaltous chloride and a novel azobenzene-containing poly(arylene ether) (PAE-azo-DCN) via a nucleophilic substitution polycondensation based on a novel bisfluoro monomer, 4-[(3,4-cyanophenyl)diazanyl]phenyl-2,6-difluorobenzoate. The obtained polymers were characterized and evaluated by FT-IR, ¹H NMR, DSC and TGA. PAE-azo-CoPc exhibited higher glass transition temperature and better thermal stability than PAE-azo-DCN because of the introduction of cobalt phthalocyanine groups. The results of Z-scan measurements demonstrated that PAE-azo-CoPc showed reversible saturable absorption and positive refraction, and PAE-azo-DCN showed saturable absorption and negative refraction. By calculation, PAE-azo-CoPc exhibited larger third-order nonlinear optical susceptibilities than that of PAE-azo-DCN. The results of optical limiting measurements demonstrated that the PAE-azo-CoPc exhibited an excellent optical limiting response.

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1. Introduction

With the fast development of laser technology, optical limiting materials, which could protect optical sensors and human eyes from harmful laser pulses, have received considerable attention.^{1–4} Many kinds of optical limiting materials such as carbon nanotubes, graphene, azo-polymer, porphyrins, phthalocyanines and metal nanoparticles have been studied.^{5–12} A perfect optical limiting material requires fast response time, low limiting threshold, large nonlinear optical susceptibilities and high transmittance for low intensity ambient light.^{13,14} In addition, excellent mechanical properties and thermal stabilities are also necessary. Up to now, developing ideal optical limiting materials is still a challenge.

Polymers containing push–pull type azobenzene chromophores have received considerable attention due to their large third-order nonlinear susceptibility of the push–pull type azobenzene chromophores.^{15,16} The push–pull type azobenzene chromophores exhibit excellent third-order nonlinear optical properties because of their conjugate π -electron systems and good fluidity of π electrons. Unless these, the easy processing and good mechanical properties of azo-polymers are also the reason why they have been considered as promising third-order nonlinear optical materials.

Phthalocyanines (Pcs) was one of the most promising optical limiting materials because of their large nonlinear susceptibility.^{17–19} It is reported that the combination of azobenzene and phthalocyanines possessed the advantages of the two constituents and showed larger nonlinear optical properties than that of phthalocyanines in small molecules.²⁰ However, it is difficult to fabricate optical devices with single phthalocyanines molecule, so many kinds of polymers have been selected as solid state matrices for phthalocyanines.^{21–23} However, the direct doping of phthalocyanines and polymers usually brings about poor dispersion and aggregation, which could lead to undesirable performance. In addition, most of the polymer matrices are vulnerable to high energy density laser due to their inferior thermal stabilities. Introducing the phthalocyanines into polymers with good thermal stability by covalent bond may be a helpful strategy to solve these problem.^{24,25}

Poly(arylene ether)s (PAEs) are a family of high-performance polymers with excellent thermal and mechanical properties. Functionalized PAEs have received considerable attention due to their potential applications in optical storage materials, fluorescent materials and proton-exchange membrane.^{26–29} However, only a little nonlinear optical materials and optical limiting materials based on PAEs have been reported,^{30–32} which need more development and research. In this paper, a novel optical limiting material with good thermal stability was designed and synthesized by introducing azobenzene chromophores and cobalt phthalocyanines into PAEs system. Firstly,

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azobenzene-containing poly(aryl ether) (PAE-azo-DCN) was prepared *via* a nucleophilic aromatic substitution polycondensation based on a novel bisfluoro monomer, 4-[(3,4-cyanophenyl)diazanyl]phenyl-2,6-difluorobenzoate. Then, poly(arylene ether)s with aromatic azo-coupled cobalt phthalocyanines in the side chain (PAE-azo-CoPc) was prepared by PAE-azo-DCN, 1,2-benzodinitrile and cobaltous chloride anhydrous. The obtained polymers were characterized and evaluated by UV-vis, ^1H NMR, DSC and TGA. The third-order optical properties of PAE-azo-DCN and PAE-azo-CoPc were evaluated by Z-scan. And the optical limiting property of PAE-azo-CoPc was also investigated.

2. Materials

2.1. Materials

4-Aminophthalonitrile was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. 2,6-Difluorobenzoyl chloride was purchased from Ruiding Chemicals Co., Ltd. 4,4'-(Hexafluoroisopropylidene)diphenol (bisphenol AF) was purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Cobalt phthalocyanine, cobalt(II) chloride, triethylamine and 1,2-dicyanobenzene were purchased from Aladdin Chemistry Co. Ltd. All the solvents were purchased from commercial sources.

2.2. Measurements

^1H NMR spectra were recorded on a Mercury-Vx300-NMR instrument using DMSO- d_6 as solvent, and the chemical shifts (δ) were given in ppm using TMS as internal reference. FT-IR spectra (KBr pellet) were recorded on a Perkin Elmer Spectre one FT-IR spectrophotometer. UV-visible absorption spectra were recorded on a Shimadzu UV-2501 UV-vis spectrophotometer. Glass transition temperatures (T_g s) were determined by a Model Mettler DSC instrument under nitrogen atmosphere at a heating rate of 20 $^\circ\text{C}$ min. Thermo-gravimetric analysis was performed on a Perkin Elmer Pyris 1 TGA analyzer with a heating rate of 10 $^\circ\text{C}$ min and under nitrogen atmosphere.

The nonlinear optical property of the sample was evaluated by a Z-scan technique performed using a Q-switched ns Nd:YAG laser system continuum with pulse width of 5 ns at 10 Hz repetition rate and 532 nm wavelength. The solution of the sample was contained in a 2 mm quartz cell and moved along the axis of the incident beam (z direction). The incident and transmitted energies were detected simultaneously by an energy meter (Laser Probe, Rj-7620 ENERGY RATIONOMETER, RjP-735). The optical limiting property was performed with the same Z-scan technique 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. The input energy was 16.5 μJ .

2.3. Synthesis

2.3.1. Synthesis of 4-((3,4-dicyanophenyl)diazanyl)phenol (monomer 1) (monomer 1, Scheme 1). Monomer 1 was synthesized as follow. Hydrochloric acid (0.4 mol, 33.6 mL) was added into the mixture of 4-aminophthalonitrile (14.315 g, 0.1

mol) and 300 mL water. Then an aqueous solution of NaNO_2 (6.9 g, 0.1 mol) was added at 0–5 $^\circ\text{C}$. The obtained solution was filtered and added into a mixture of NaOH (8.0 g, 0.2 mol), phenol (9.4 g, 0.1 mol), and NaHCO_3 (25.2 g, 0.3 mol) in 200 mL water. After the obtained mixture was stirred at 0–5 $^\circ\text{C}$ for 1 h, hydrochloric acid (0.4 mol, 33.6 mL) was added into the final mixture. The resulting precipitate was collected and dried. The crude product was recrystallized from ethanol (yield: 58%). IR (KBr, cm^{-1}): 2239 (–CN), 3327 (–OH); ^1H NMR (DMSO- d_6 , δ , ppm): 10.75 (s, 1H), 8.44 (d, 1H), 8.30 (d, 1H), 8.21 (d, 1H), 7.89 (d, 2H), 6.99 (d, 2H).

2.3.2. 4-((3,4-Dicyanophenyl)diazanyl)phenyl-2,6-difluorobenzoate (monomer 2, Scheme 1). Under N_2 atmosphere, a solution of 2,6-difluorobenzoyl chloride (8.8275 g, 0.05 mol) in 30 mL CH_2Cl_2 was added dropwise into a mixture of monomer 1 (12.4125 g, 0.05 mol) and triethylamine (5 mL) in 80 mL CH_2Cl_2 . Then the mixture was refluxed for 20 h. The resulting insoluble inorganic salt was removed by filtering. After evaporating the filtrate, the crude product was recrystallized from toluene, and the monomer 2 was obtained as red crystal (yield: 67%). IR (KBr, cm^{-1}): 2231 (–CN), 1749 (–CO–); ^1H NMR (DMSO- d_6 , δ , ppm): 8.60 (s, 1H), 8.39 (d, 1H), 8.34 (d, 1H), 8.12 (d, 2H), 7.81–7.83 (m, 1H), 7.62 (d, 2H), 7.38 (t, 2H).

2.3.3. Synthesis of azobenzene-containing poly(aryl ether) (PAE-azo-DCN, Scheme 2). Bisphenol AF (3.3623 g, 0.01 mol), monomer 2 (3.8843 g, 0.01 mol), K_2CO_3 (1.5201 g, 0.011 mol), DMAc (22 mL) and toluene (10 mL) were put into a three-necked flask. The reaction mixture was refluxed at 130 $^\circ\text{C}$ for 3 h to ensure complete dehydration. After removal of toluene, the reaction mixture was heated at 150–160 $^\circ\text{C}$ for 8 h. After being poured into the deionized water, the precipitate was collected and washed with hot water and ethanol several times. The resulting product was dried at 80 $^\circ\text{C}$ under vacuum for 24 h and PAE-azo-DCN was obtained as orange powder. The yield was 83%.

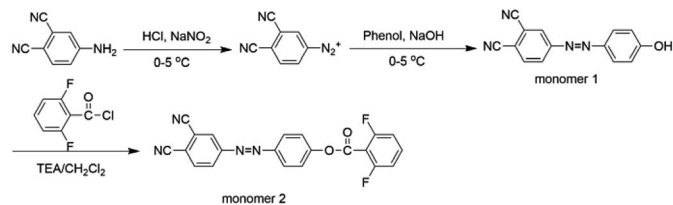
2.3.4. Azobenzene-containing poly(arylene ether)s with phthalocyanine cobalt(II) in the side chain (PAE-azo-CoPc, Scheme 2). The synthetic procedure of PAE-azo-CoPc was shown as follows. For PAE-azo-DCN (0.5205 g, 0.002 mol), 1,2-dicyanobenzene (0.436 g, 0.006 mol), CoCl_2 (0.1546 g, 0.002 mol) and quinoline (20 mL) were put into a three-necked flask. The mixture was heated at 210 $^\circ\text{C}$ for 8 h under nitrogen atmosphere. After being poured into methanol, the precipitate was collected by filtration. The crude product was washed with acetone, ethanol and deionized water. Then the crude product was collected by filtration and extracted by chloroform with a Soxhlet extractor. The chloroform solution was concentrated and precipitated in methanol. The resulting product was dried at 100 $^\circ\text{C}$ under vacuum for 24 h and PAE-azo-CoPc was obtained.

3. Results and discussion

3.1. Synthesis and characterization

We designed a new bisfluoro monomer (monomer 2) containing azobenzene group and the synthetic route of the monomer is illustrated in Scheme 1. The structure of monomer 2 was confirmed by IR and ^1H NMR, as shown in Fig. 1 and 2. The IR





Scheme 1 Synthetic route of monomer 1 and monomer 2.

spectrum showed the characteristic bands of $-\text{CN}$, C-F and $-\text{CO}-$ stretching vibrations at 2231, 1013 and 1748 cm^{-1} , respectively. It also could be observed the characteristic bands of $-\text{C}=\text{C}-$ of benzene at 1624 cm^{-1} and 1588 cm^{-1} . In the ^1H NMR spectrum of monomer 2, all of the signals are well agreement with the expected structure.

PAE-azo-DCN and PAE-azo-CoPc were synthesized as shown in Scheme 2. From Table 1, it could be seen that both PAE-azo-DCN and PAE-azo-CoPc had number average molecular weights above $1 \times 10^4 \text{ g mol}^{-1}$. Both PAE-azo-DCN and PAE-azo-CoPc showed good solubility in common organic solvents such as tetrahydrofuran, cyclohexanone, dimethylacetamide, *N,N*-dimethylformamide and *N*-methyl-2-pyrrolidone.

The chemical structures of PAE-azo-DCN and PAE-azo-CoPc were confirmed by ^1H NMR and UV-vis spectra. Fig. 3 shows

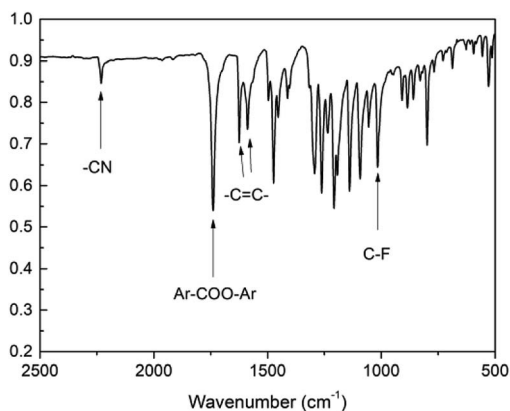
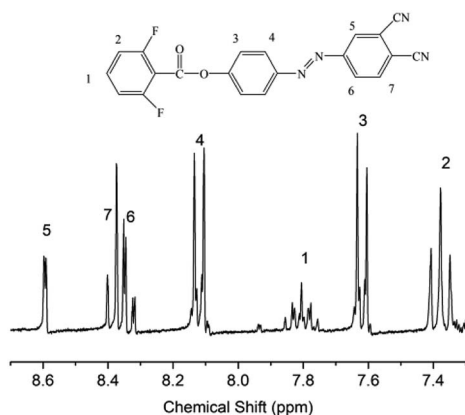
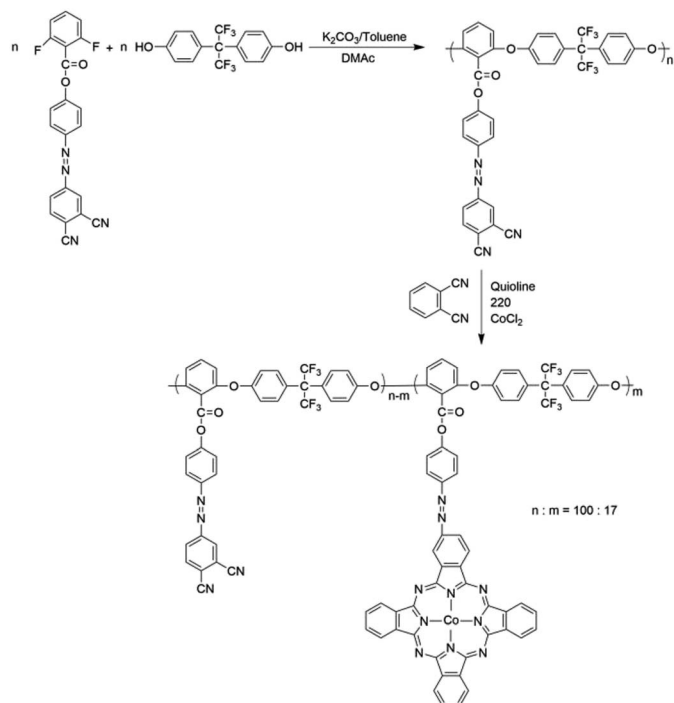


Fig. 1 IR (KBr) spectrum of monomer 2.

Fig. 2 ^1H NMR spectrum of monomer 2 in DMSO-d_6 .

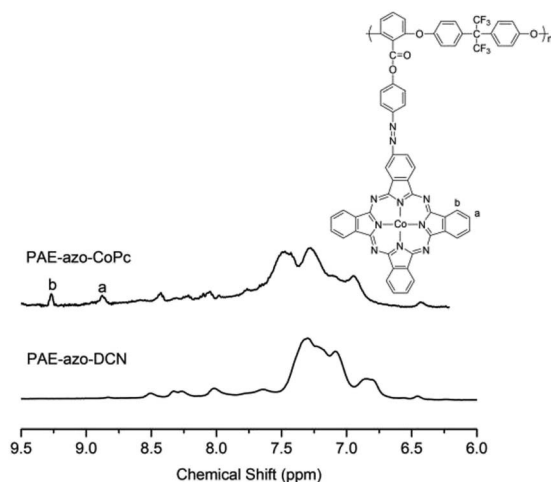
Scheme 2 Synthesis routes to PAE-azo-DCN and PAE-azo-CoPc.

Table 1 Properties of PAE-azo-DCN and PAE-azo-CoPc

Polymer	M_n	M_w/M_n	T_g^a ($^{\circ}\text{C}$)	T_{a5}^b ($^{\circ}\text{C}$)
PAE-azo-DCN	1.01×10^4	1.5	158	381
PAE-azo-CoPc	1.05×10^4	2.1	164	387

^a Glass transition temperature by DSC. ^b 5% weight-loss temperatures were detected at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ in nitrogen.

typical ^1H NMR spectra of PAE-azo-DCN and PAE-azo-CoPc in DMSO-d_6 with signal assignment. Compared to the ^1H NMR spectrum of PAE-azo-DCN, it was observed that the signals of protons a and b appear at δ 9.28 and 8.87 ppm in the spectrum of

Fig. 3 ^1H NMR spectra of PAE-azo-DCN and PAE-azo-CoPc.

PAE-azo-CoPc. The grafting ratio of the phthalocyaninecobalt unites is about 17% as estimated from the NMR characterization. The UV-vis spectra of PAE-azo-DCN and PAE-azo-CoPc in DMF solution are shown in Fig. 4. As shown in Fig. 4, the characteristic absorption bands at around 360 nm could be observed which corresponded to $\pi-\pi^*$ transitions resulted from the intramolecular charge transfer of the azobenzene groups. Compared to the UV-vis spectrum of PAE-azo-DCN, the UV-vis spectrum of PAE-azo-CoPc showed a new peak at around 664 nm corresponding to the characteristic absorption bands of phthalocyaninecobalt unites.

3.2. Thermal properties of PAE-azo-DCN and PAE-azo-CoPc

Fig. 5 shows the DSC curves of the polymers, and the corresponding experimental data are listed in Table 1. Due to the aromatic structure, both PAE-azo-DCN and PAE-azo-CoPc showed high T_g s. Compared to the T_g of PAE-azo-DCN, T_g of PAE-azo-CoPc increased from 158 °C to 163 °C after the introduction of phthalocyaninecobalt groups. Fig. 6 shows the TGA analysis curves of PAE-azo-DCN and PAE-azo-CoPc, and the detailed experimental data from the TGA analysis are also listed in Table 1. From Fig. 6 and Table 1, it could be observed that both of the 5% weight loss (T_{d5}) of PAE-azo-DCN and PAE-azo-CoPc were

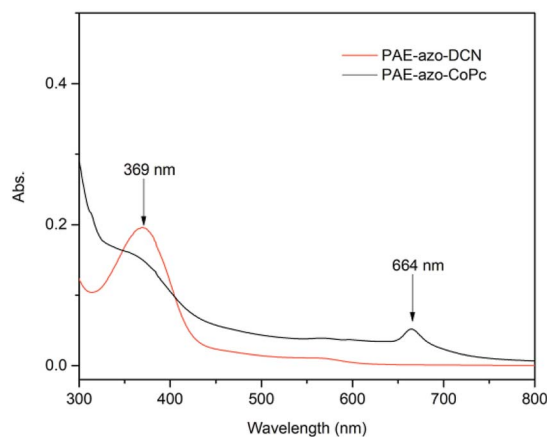


Fig. 4 UV-vis spectra of PAE-azo-DCN and PAE-azo-CoPc in DMF solution.

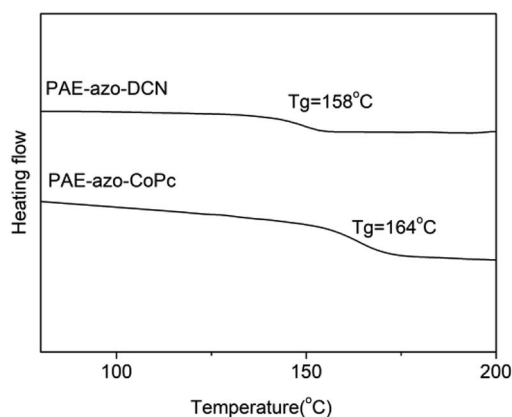


Fig. 5 DSC curves of PAE-azo-DCN and PAE-azo-CoPc.

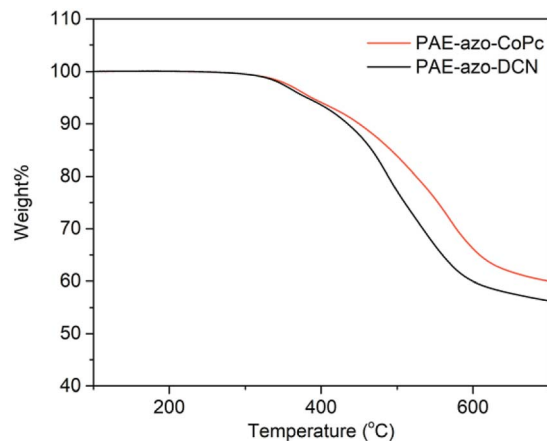


Fig. 6 TGA curve of PAE-azo-DCN and PAE-azo-CoPc in nitrogen.

above 380 °C, indicating their good thermal stability. Compared to T_{d5} of PAE-azo-DCN, T_{d5} of PAE-azo-CoPc increased from 381 °C to 387 °C after the introduction of phthalocyaninecobalt groups. Compared to the other azo-polymer optical limiting materials,^{33–36} both of PAE-azo-DCN and PAE-azo-CoPc showed better thermal stabilities, which could be attributed to the aromatic rigid structure of poly(arylene ether)s and phthalocyanines.

3.3. Transparency of the films of the polymers

To verify the feasibility of the material application, the films of the polymers was prepared as follow. The polymers were dissolved in dried DMF (10 wt%). After stirring for 1 h, the solution was filtered through 0.45 μm syringe filter membranes. The films were obtained *via* spin-coating the solution onto clean silica glass substrates. After drying under vacuum for 24 h, the films were obtained. The transparency of the films was measured with a Shimadzu UV-2501 UV-vis spectrophotometer. The films were about 5 μm thick. As shown Fig. 7, the films of the polymers showed good transmittance (above 40%) at 450–800 nm.

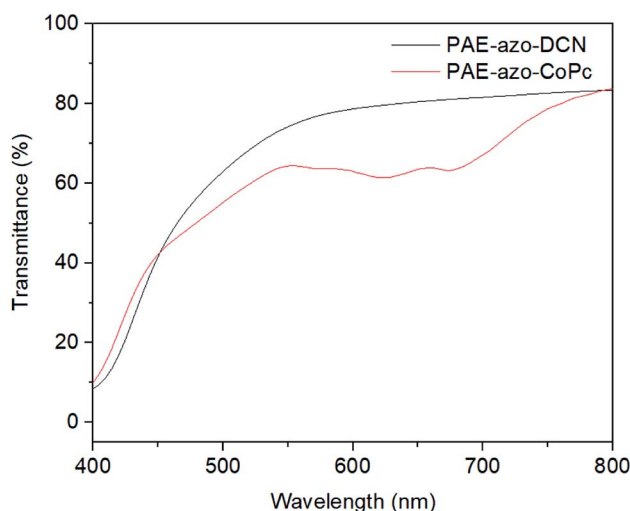


Fig. 7 The transmittance (%) of the films of the polymers.



3.4. Nonlinear optical properties

The nonlinear absorption coefficients of the polymers in DMF were measured using Z scan technique. As shown in Fig. 8, the results of Z scan with and without an aperture indicated that all the polymers had both nonlinear absorption and refraction. Thus, the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of the polymers should be attributed to nonlinear absorption (α_2) and refractive (n_2). The nonlinear absorption coefficient α_2 of the polymers can be determined by the experimental data based on eqn (1) and (2):

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

$$q_0(z) = \alpha_2 I_0(t) L_{\text{eff}} / (1 + z_2 + z_0^2) \quad (2)$$

In the equation, $I_0(t)$ was the intensity of laser beam at focus ($z = 0$); $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)] / \alpha_0$ was the effective thickness; α_0 was the linear absorption coefficient; L was the sample thickness; z was the sample position; z_0 was the diffraction length of the beam. The curves in Fig. 8(a) and (c) are obtained from eqn (1) and (2). As shown in Table 2, the nonlinear absorption coefficient α_2 of PAE-azo-DCN was -6×10^{-11} esu which corresponded to saturable absorption, and the nonlinear absorption coefficient α_2 of PAE-azo-CoPc was 2×10^{-10} esu which corresponded to reverse saturable absorption of cobalt phthalocyanine.

$$T(z, \Delta\Phi) = 1 + \frac{4\Delta\Phi x}{(x^2 + 9)(x^2 + 1)} \quad (3)$$

The nonlinear refractive coefficient n_2 of the polymers can be determined by the experimental data based on eqn (3). In the equation, $x = z/z_0$ and $\Delta\Phi$ is the on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\Phi = [2\pi I_0(1 - e^{-\alpha_0 L})n_2] / (\lambda\alpha_0)$. The curves in Fig. 8(b) and (d) are obtained from eqn (3). As shown in Table 2, the nonlinear refractive coefficient n_2 of PAE-azo-DCN was -2.5×10^{-17} , and the nonlinear refractive coefficient n_2 of PAE-azo-CoPc was 3×10^{-17} .

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

The $\chi^{(3)}$ can be calculated by the eqn (4). In the equation, ε_0 is the permittivity of vacuum; c is the speed of light; n_0 is the refractive index of the medium; $\omega = 2\pi c/\lambda$. By calculated from eqn (4), the nonlinear susceptibilities of PAE-azo-CoPc and PAE-azo-DCN are 5.18×10^{-11} esu and 4.27×10^{-11} esu, respectively. The reason of the improving of nonlinear susceptibilities was the introduction of phthalocyaninecobalt groups. In addition, both of the two polymers showed larger nonlinear susceptibilities than those of other azobenzene-containing poly(aryl ether) (azo-PAE)²⁹ or other azo-polymer systems.^{37–39} The increase of the nonlinear susceptibilities could be attributed to the aromatic rigid structure of poly(arylene ether)s and the large conjugated structure of the phthalocyanine.

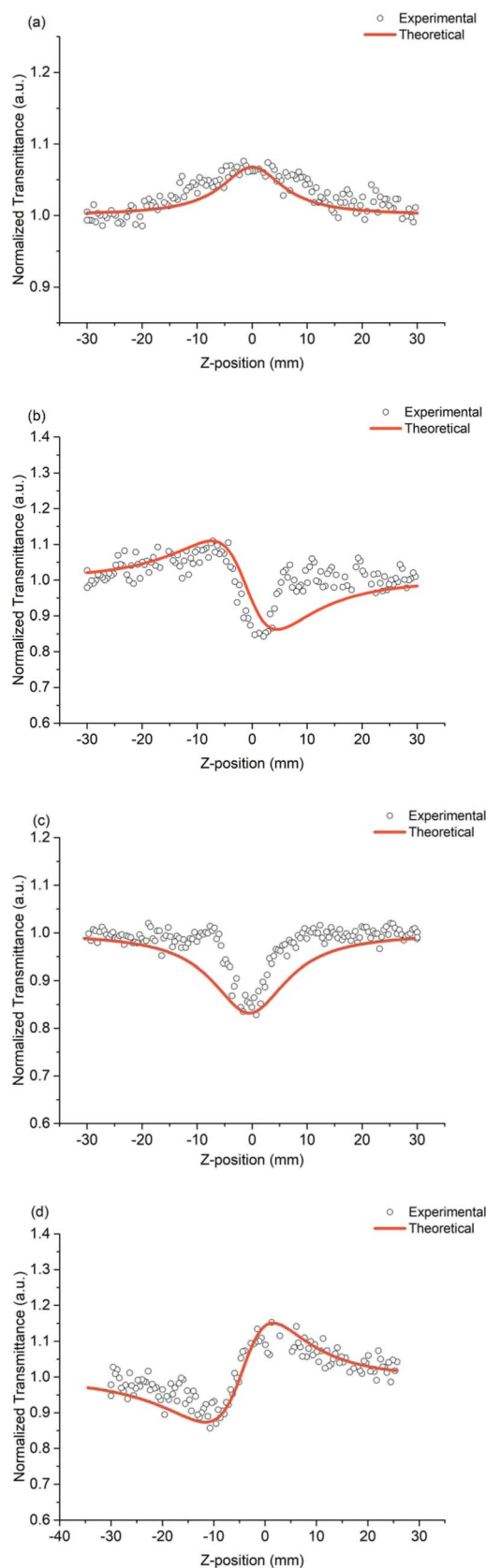


Fig. 8 Z-scan data of (a) PAE-azo-DCN (open aperture), (b) PAE-azo-DCN (close aperture), (c) PAE-azo-CoPc (open aperture), and (d) PAE-azo-CoPc (close aperture).



Table 2 Nonlinear Properties of PAE-azo-DCN and PAE-azo-CoPc

Polymer	α_2	n_2	$\chi^{(3)}$
PAE-azo-DCN	-6×10^{-11}	-2.5×10^{-17}	4.27×10^{-11}
PAE-azo-CoPc	2×10^{-10}	3×10^{-17}	5.18×10^{-11}

3.5. Optical limiting properties

The optical limiting performance of PAE-azo-CoPc were measured in DMF with the same Z-scan technique system as in the nonlinear absorption experiment. The curves of normalized transmittance *versus* input fluence of PAE-azo-CoPc was show in Fig. 9. As shown in Fig. 9, PAE-azo-CoPc showed well OL performance with the limiting threshold (incident fluence at which the transmittance falls to 50% of the linear transmittance) of 0.038 J cm^{-2} . The curves of output fluence *versus* input fluence of PAE-azo-CoPc was show in Fig. 10. As shown in Fig. 10, the output fluence linearly increased with the incident fluence obeying the Beer–Lambert law at low-incident fluence. However, at high-incident fluence, the output fluence deviated from linearity, showed typical behavior of optical limiting response.

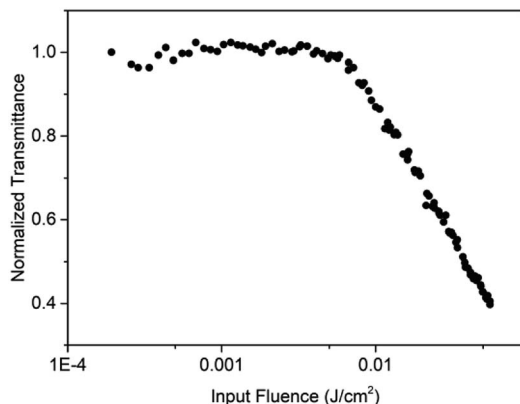
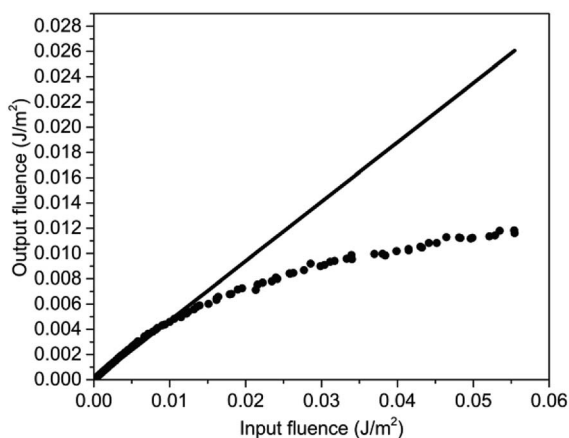


Fig. 9 Optical limiting response of PAE-azo-CoPc in DMF.

Fig. 10 The curves of output fluence *versus* input fluence of PAE-azo-CoPc in DMF.

4. Conclusions

In this work, a novel kind of poly(arylene ether)s with azo-coupled cobalt phthalocyanine in the side chain (PAE-azo-CoPc) was prepared by 1,2-benzodinitrile, cobaltous chloride anhydrous and a novel azobenzene-containing poly(aryl ether) (PAE-azo-DCN). Both of the polymers exhibited high glass transition temperature ($T_g > 158 \text{ }^\circ\text{C}$) and good thermal stability ($T_{d5} > 380 \text{ }^\circ\text{C}$). PAE-azo-CoPc exhibited higher glass transition temperature and better thermal stability than PAE-azo-DCN due to the introduction of cobalt phthalocyanine groups. The results of Z-scan measurements demonstrated that PAE-azo-CoPc showed reverse saturable absorption and positive refraction, and PAE-azo-DCN showed saturable absorption and negative refraction. PAE-azo-CoPc exhibited larger third-order nonlinear optical susceptibilities than that of PAE-azo-DCN. The results of optical limiting measurements demonstrated that PAE-azo-CoPc showed well OL performance with the limiting threshold of 0.038 J cm^{-2} . PAE-azo-CoPc could be expected to be a potential material for optical limiting, optical switching and other optical applications. This work provided a novel path for designing new excellent optical limiting materials with good thermal stability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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