Supporting Information

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

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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. Theoretically, the nonlinear absorption coefficient $\beta$ of the materials can be determined by the fitting of the experimental data based on equation (1).49

$$T(z, s=1) = \sum_{m=0}^{\infty} \left( \frac{q_0(z)}{z_0} \right)^m$$

Here $q_0(z) = \beta I_0(t)L_{eff}/(1+z^2/z_0^2)$, $I_0(t)$ is the intensity of laser beam at focus ($z = 0$), $L_{eff} = [1-\exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness, $\alpha_0$ is the linear absorption coefficient, $L$ is the sample thickness, $z_0$ is the diffraction length of the beam, and $z$ is the sample position. Thus, the nonlinear absorption coefficients of the polymers can be determined by fitting the experimental data with equation (1). The nonlinear refractive coefficients ($n_2$) of the polymers can be determined by fitting the experimental data using equation (2).49

$$T(z, \Delta \Phi) = 1 + 4\Delta \Phi \times (x^2 + 9)(x^2 + 1)$$

Where $x = z/z_0$ and $\Delta \Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta \Phi = 2\pi I_0(1-e^{-\alpha L})n_2/\alpha_0$.

In accordance with the observed $\beta$ and $n_2$ values, the third order susceptibility $\chi^{(3)}$ value can be calculated through the following equation:

$$|\chi^{(3)}| = \frac{10^{-6} c \varepsilon_0 n_0^2 \beta}{80\pi n_2}$$

Where $\varepsilon_0$ is the permittivity of vacuum, $c$ is the speed of light, $n_0$ represents the refractive index of the medium, and $\varepsilon = 2\pi c/\lambda$. The calculated results of the nonlinear optical coefficients for all the samples in THF were summarized in Table 3.
Fig. S1 IR spectra of (a) PAEK-COOH30%-TPP (b) PAEK-COOH30%-TTP, and (c) PAEK-COOH50%-TNP.

Fig. S2 $^1$H NMR spectra of (a) OH-TPP, (b) OH-TTP, and (c) OH-TNP.
Fig. S3 $^1$H NMR spectra of (a) PAEK-COOH30%-TPP, (b) PAEK-COOH30%-ZnTPP, and (c) PAEK-COOH30%-PbTPP.

Fig. S4 EDS mapping photographs of (a) PAEK-COOH30%-ZnTPP and (b) PAEK-COOH30%-PbTPP. The red/green dots represented the position of Zn/Pb element.
Fig. S5 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. S6 Normalized closed Z-scan curves of (a) PAEK-COOH30%-TPP, (b) PAEK-COOH30%-ZnTPP, and (c) PAEK-COOH30%-PbTPP.
Fig. S7 Optical limiting responses of PAEK-COOH10%-TPP, PAEK-COOH30%-TPP, and PAEK-COOH50%-TPP at the same concentration of 0.25 mg/mL at 532 nm in THF.