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 openaperture and closed-aperture configuration with 4 ns pulsed laser irradiation at 532 nm with an intensity of 5.3 μ J. Theoretically, the nonlinear absorption coefficient β of the materials can be determined by the fitting of the experimental data based on equation (1).⁴⁹

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

Here $q_0(z) = \beta I_0(t) L_{\text{eff}}/(1+z^2/z_0^2)$, $I_0(t)$ is the intensity of laser beam at focus (z = 0), $L_{\text{eff}} = [1-\exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness, α_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

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

(2)

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

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

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

Where ε_0 is the permittivity of vacuum, *c* is the speed of light, n_0 represents the refractive index of the medium, and $\omega = 2\pi c/\lambda$.⁴⁹ The calculated results of the nonlinear optical coefficients for all the samples in THF were summarized in Table 3.

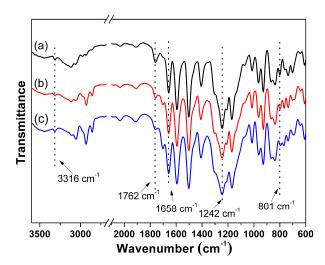


Fig. S1 IR spectra of (a) PAEK-COOH30%-TPP (b) PAEK-COOH30%-TTP, and (c) PAEK-COOH50%-TNP.

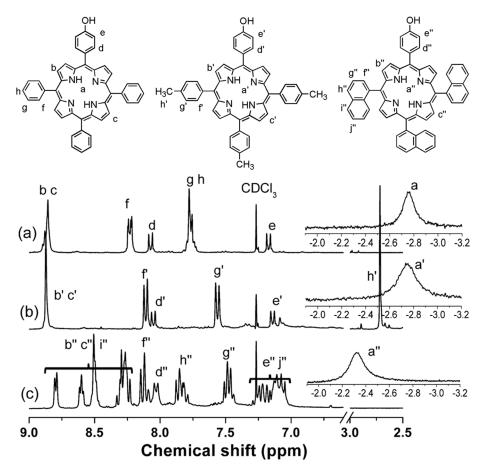


Fig. S2 ¹H NMR spectra of (a) OH-TPP, (b) OH-TTP, and (c) OH-TNP.

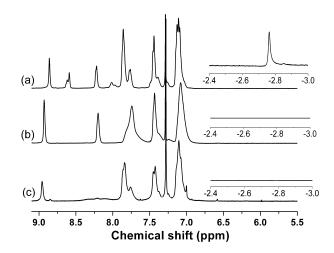


Fig. S3 ¹H NMR spectra of (a) PAEK-COOH30%-TPP, (b) PAEK-COOH30%-ZnTPP, and (c) PAEK-COOH30%-PbTPP.

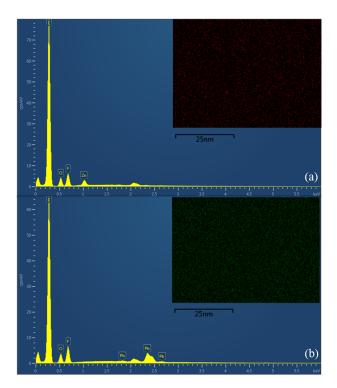


Fig. S4 EDS mapping photographs of (a) PAEK-COOH30%-ZnTPP and (b) PAEK-COOH30%-PbTPP. The red/green dots represented the position of Zn/Pb element.

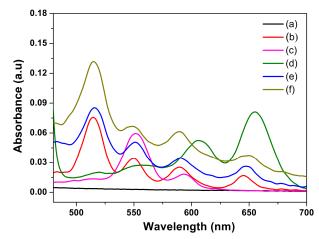


Fig. S5 UV-vis absorption spectra of (a) PAEK-COOH30%, (b) PAEK-COOH30%-TPP, (c) PAEK-COOH30%-ZnTPP, (d) PAEK-COOH30%-PbTPP, (e) PAEK-COOH30%-TTP, and (f) PAEK-COOH30%-TNP.

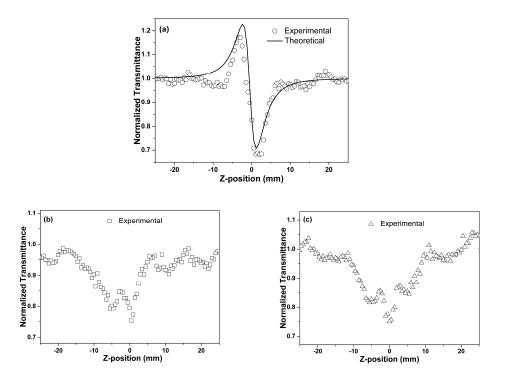


Fig. S6 Normalized closed Z-scan curves of (a) PAEK-COOH30%-TPP, (b) PAEK-COOH30%-ZnTPP, and (c) PAEK-COOH30%-PbTPP.

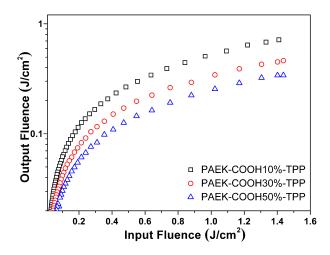


Fig. S7 Optical limiting responses of PAEK-COOH10%-TPP, PAEK-COOH30%-TPP, and PAEK-COOH50%-TPP at the same concentration of 0.25 mg/mL at 532 nm in THF.