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Nonlinear Optical Properties of a New Porphyrin-Containing Polymer

Arun K. Sinha, Bipin Bihari, and Braja K. Mandal*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

Lin Chen

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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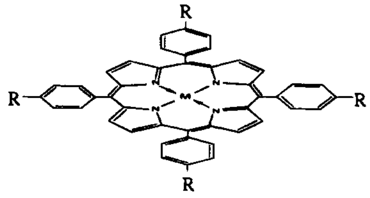
Introduction

There is currently a great interest in polymeric thin films containing high concentrations of cyclic π-conjugated systems in the areas of laser-pumped electrooptical devices,[1] sensors,[2] and optical limiters for the protection against short and intense laser pulses.[3] It is predicted that polymeric films containing high concentrations of π-conjugated chromophores will lead to useful properties such as high nonlinear optical susceptibility.[4] Although the tetraphenylporphyrin (TPP) system which contains extended cyclic π-conjugation has been the subject of numerous research investigations in past decades, only a few accounts of TPP polymeric films have been reported.[5] Most TPP polymers were made by derivatization through the para positions of the phenyl rings, and thin film processing often proved problematic due to the poor solubility of these derivatives in common organic solvents. To our knowledge, there has yet to be reported a TPP derivative soluble in concentrations of over 20% (w/w) in organic solvents. Moreover, little effort has been made to incorporate high concentrations of covalently linked TPP rings into a polymer that is processable into thin films. Covalent attachment of TPP rings with the polymer matrix is essentially required to avoid phase segregation and formation of microcrystals which result in polymeric films unsuitable for practical applications.

Spin-on-glass (SOG),[6] a reactive polysiloxane, has been used by several research groups for electronic applications.[7] The polymer contains pendant reactive ethoxy groups which undergo cross-linking on heating, leading to a glasslike, hard, amorphous film. Since most TPP derivatives containing reactive functional groups (e.g., hydroxyl or carboxyl groups) are sparingly soluble in common organic solvents, we decided to make a reactive TPP derivative that will be compatible with SOG. We postulated that the presence of several reactive ethoxysilane groups on a TPP ring not only will take part in the cross-linking process but also will improve solubility in the SOG solution.[8] Here we describe a convenient synthetic route to obtain a highly soluble TPP derivative (**1**) that is processable into optical quality thin films with SOG.

Results and Discussion

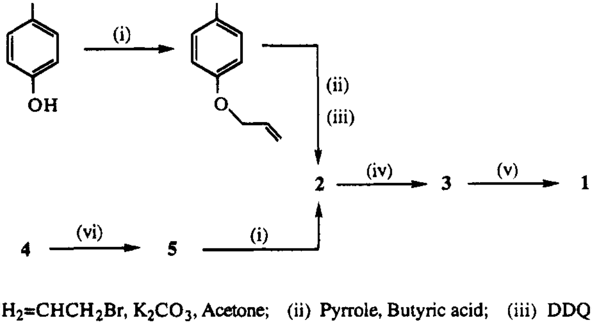
The TPP derivative **1** which contains four reactive triethoxysilane groups was prepared by hydrosilylation of allyloxy-TPP derivative **2** using triethoxysilane in the presence of a catalytic amount of chloroplatinic acid.[9] Compound **2** was prepared by two routes (Scheme 1). In one method the cyclization of 4-(allyloxy)benzaldehyde (synthesized by allylation of 4-hydroxybenzaldehyde with allyl bromide) and pyrrole was performed to construct a TPP ring following a standard procedure described elsewhere.[10,11] Due to low yield of cyclization (ca. 13%), we developed another route using a commercially available TPP derivative **4**. The two-step process, demethylation[12] and allylation, produces **2** in an overall yield of 60%. Preparation of zinc complex **3** was necessary prior to hydrosilylation since the hydrosilylation of metal-free porphyrin **2** was not successful due to the formation of an insoluble, green-colored complex salt in the presence of chloroplatinic acid. The metalation was carried out by treatment of **2** with zinc acetate in DMF.[13] The assigned structures of all TPP derivatives were supported by the analytical data.



	M	R
1	Zn	OCH$_2$CH$_2$CH$_2$Si(OEt)$_3$
2	2H	OCH$_2$CH=CH$_2$
3	Zn	OCH$_2$CH=CH$_2$
4	2H	OMe
5	2H	OH

The TPP derivative **1** was found highly soluble in common organic halogenated solvents and in SOG solution. For instance, the solubility of **1** was measured in chloroform at 23% by weight.[14] An optical quality film containing 25% of **1** (w/w) was conveniently prepared by casting a solution of **1** in SOG, followed by curing at 200 °C for 30 min under nitrogen. While the electronic spectra of all TPP derivatives showed an intense Soret band at ca. 422 nm, the Q-bands of metal-free compound **2** differed from zinc derivatives **1** and **3**. The Q-bands of **2** appeared at 519, 556, 592, and 650 nm, while the spectra of the zinc derivatives **1** and **3** showed complete disappearance of the bands at 519 and 650 nm.[15] The cured polysiloxane film containing **1** exhibits optical absorption characteristics similar to that of **1** in solution. The cured film was found highly thermostable as indicated by thermogravimetric analysis (Figure 1). High thermostability is desirable in optical limiting applications where the film experiences heat gain due to absorption of laser light. The cured

Scheme 1



(i) CH$_2$=CHCH$_2$Br, K$_2$CO$_3$, Acetone; (ii) Pyrrole, Butyric acid; (iii) DDQ; (iv) Zn(OAc)$_2$, DMF; (v) HSi(OEt)$_3$; H$_2$PtCl$_6$; (vi) BBr$_3$, CHCl$_3$, -78°C.

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* To whom all correspondence should be addressed.

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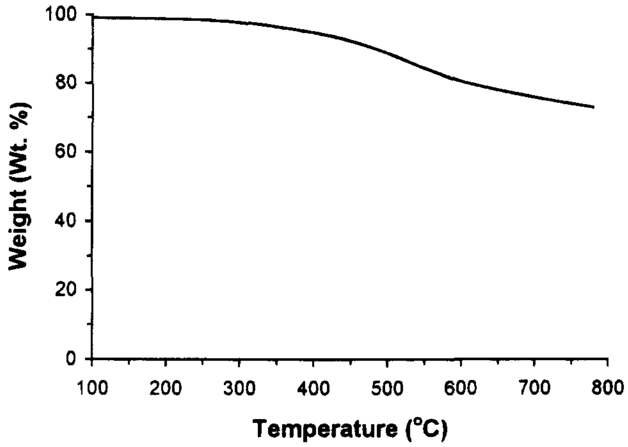

Figure 1. TGA trace of a cured TPP−SOG polymer film.

Table 1. Nonlinear Optical Properties of the TPP Derivative

	wavelength (nm)	$\langle\gamma\rangle$ (esu)	$\chi^{(3)}$ (esu)
solution	532	24.49×10^{-32}	3.06×10^{-10}
	1064	2.81×10^{-32}	0.36×10^{-10}
film	532	60.10×10^{-32}	3.25×10^{-10}

polymer film was also found resistant to solvent attack as indicated by the absence of surface damage upon immersing the film in chloroform for several hours.

The degenerate four-wave mixing (DFWM) technique[4] in the conventional counterpropogating pump beam geometry has been used to determine the third-order nonlinear susceptibility, $\chi^{(3)}$, of the TPP derivative. The details of the experimental setup have been reported previously.[16] The measurements were carried out with both TPP−SOG films and dioxane solutions. The $\chi^{(3)}$ of the TPP derivative compared to CS_2 was calculated using the following equation:[17,18]

$$\chi^{(3)} = \chi^{(3)}_{\mathrm{CS}_2}\left(\frac{I_{\mathrm{pc}}/(I_0)^3}{I_{\mathrm{pc,CS}_2}/(I_{0,\mathrm{CS}_2})^3}\right)^{1/2}\left(\frac{n}{n_{\mathrm{CS}_2}}\right)^2\frac{l_{\mathrm{CS}_2}}{l}\left(\frac{\alpha l}{e^{-\alpha l/2}(1-e^{-\alpha l})}\right) \qquad (1)$$

where I_{pc} and I_0 are the intensities of the phase-conjugated signal and the signal proportional to the laser intensity; l is the interaction path length; n is the refractive index of the medium; and α is the absorption coefficient of the sample at the laser wavelength in rec. The $\chi^{(3)}$ value of CS_2 was taken as 6.8×10^{-13} esu.

The second hyperpolarizability $\langle\gamma\rangle$ of the TPP derivative was calculated from the slope of the straight line fit obtained by plotting $\chi^{(3)}$ data of dioxane solutions with respect to concentrations.[19] The results are summarized in Table 1. Since the TPP derivative exhibits slight absorption at 532 nm, the observed $\chi^{(3)}$ value is believed to be resonance enhanced (Figure 2). In view of this we performed the same experiment at 1064 nm where the TPP derivative shows complete optical transparency. The results indicate that the resonance-enhanced $\chi^{(3)}$ value is about 8 times higher compared with that of the nonresonance one.

Experimental Part

4-(Allyloxy)benzaldehyde. A 250-mL three-necked round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 4-hydroxybenzaldehyde (48.84 g, 0.40 mol), anhydrous K_2CO_3 (57 g, 0.413 mol), and acetone (200 mL) and stirred for 15 min. Allyl bromide (50 g, 0.413 mol) in 25 mL of acetone was added slowly over a period of 15 min, and the mixture was refluxed for 24 h under nitrogen. The resulting solution was then poured into water, extracted with ether (50 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was evaporated to obtain a pale yellow oil. Yield: 59.19 g (91%). The product was used in the next step without further purification. For the purpose of analysis, a small amount of the compound was chromatographed over silica gel (benzene). Anal. Calcd for $C_{10}H_{10}O_2$: C, 70.06; H, 6.21. Found: C, 69.87; H, 6.06. FT-IR (neat, cm^{-1}): 3374 (w), 2924 (vs), 2855 (vs), 2730 (m), 1697 (vs), 1601 (vs), 1579 (s), 1509 (s), 1459 (s), 1377 (m), 1311 (m), 1257 (vs), 1161 (s), 1111 (m), 966 (m), 929 (m), 857 (m), 832 (vs), 763 (w), 722 (m), 657 (m), 597 (m). ^1H-NMR ($CDCl_3$): δ 4.61 (m, 2H, $C{=}CH_2$), 5.38 (m, 2H, OCH_2), 6.04 (m, 1H, $C{=}CH$), 6.99, 7.82 (dd, 4H, C_6H_4).

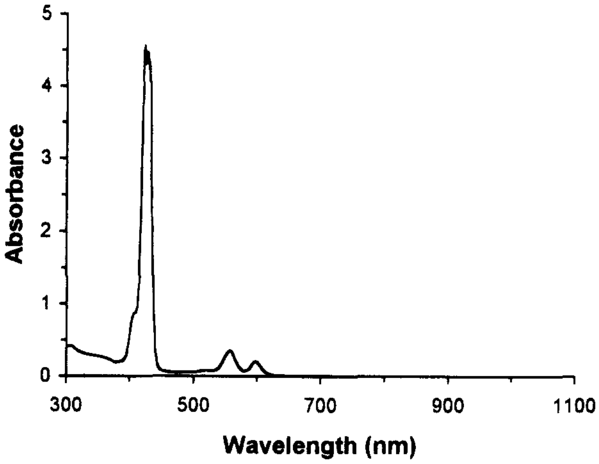

Figure 2. UV−vis spectrum of **1** in dioxane.

Method a: *meso*-Tetrakis[4-(allyloxy)phenyl]porphyrin (2). 4-(Allyloxy)benzaldehyde (53.53 g, 0.33 mol) in butyric acid (500 mL) was brought to reflux under nitrogen. Pyrrole (22.14 g, 0.33 mol) was then added and reflux continued for 3 h. The reaction mixture was allowed to cool to room temperature and kept overnight in a refrigerator. The solid was filtered, washed with hot water (70 mL × 3) to remove traces of butyric acid, and dried at 60 °C in a vacuum oven. The solid was further treated with dichlorodicyanoquinone (DDQ; 3 g, 0.013 mol) in 100 mL of methanol, and the solution was refluxed for 1 h. The crude product was filtered from the cooled solution and purified by Soxhlet extractions with acetonitrile (fraction discarded) and dichloromethane (fraction collected and evaporated). Further purification was done by column chromatography over silica gel (dichloromethane). Yield: 9.1 g (13%). Anal. Calcd for $C_{56}H_{46}N_4O_4$: C, 80.16; H, 5.53; N, 6.68. Found: C, 79.76; H, 5.49; N, 6.48. FT-IR (KBr, cm^{-1}): 3435 (br), 3082 (w), 3027 (w), 2927 (w), 2706 (w), 1605 (s), 1506 (vs), 1473 (s), 1350 (m), 1291 (s), 1241 (vs), 1175 (vs), 1120 (w), 1024 (m), 966 (m), 926 (m), 804 (vs), 740 (m). ^1H-NMR ($CDCl_3$): δ −2.75 (s, 2H, NH), 4.78 (m, 8H, $C{=}CH_2$), 5.57 (m, 8H, OCH_2), 6.24 (m, 4H, $C{=}CH$), 7.25, 8.09 (dd, 16H, C_6H_4), 8.85 (s, 8H, β-pyrrole). UV−vis ($CHCl_3$, nm): 422, 519, 556, 592, 650.

Method b: *meso*-Tetrakis(4-hydroxyphenyl)porphyrin (5). **4** (7.5 g, 0.0102 mol; Aldrich) dissolved in 40 mL of dichloromethane was added dropwise into BBr_3 (9 mL, 0.095 mol) in dry dichloromethane (15 mL) at −78 °C over a period of 1.5 h. The mixture was warmed slowly to room temperature and stirred overnight. The reaction mixture was then cooled to 0 °C, poured slowly into ice water (500 mL) to hydrolyze unchanged BBr_3, and neutralized with triethylamine. The crude product was filtered, washed with hot water, and dried. Further purification was performed by Soxhlet extractions with dichloromethane (fraction discarded) and acetone (fraction collected and evaporated). Yield: 6.06 g (88%). Anal. Calcd for $C_{44}H_{30}N_4O_4$: C, 77.86; H, 4.45; N, 8.25. Found: C, 77.46; H, 4.61; N, 7.98. FT-IR (KBr, cm^{-1}): 3457 (br), 1614 (vs), 1516 (vs), 1481 (w), 1473 (w), 1433 (m), 1399 (m), 1359 (m), 1352 (vs), 1276 (vs), 1183 (s), 1111 (m), 1075 (m), 983 (m), 968 (m), 811 (vs), 730 (w). ^{1}H NMR (DMSO-d_6/CDCl$_3$, 4:1): δ −2.88 (s, 2H, NH), 7.18, 7.96 (dd, 16H, C_6H_4), 8.86 (s, 8H, β-pyrrole), 9.88 (s, 4H, −OH). UV−vis (CHCl$_3$, nm): 418, 518, 555, 593, 650.

Compound **2** was obtained by refluxing a mixture of compound **5** (4 g, 0.006 mol), allyl bromide (11.6 g, 0.048 mol), and anhydrous K_2CO_3 (66.4 g, 0.048 mol) in acetone (200 mL) under nitrogen for 24 h. The reaction mixture was filtered and washed throughly with dichloromethane, and the filtrate was evaporated in a rotavap. The residue was washed with water, extracted with ether, and dried over anhydrous Na_2SO_4, and the solvent was evaporated. The solid product was purified by the same procedure described above. Yield: 3.4 g (70%). The analytical data were found to be similar to the product obtained by method a.

***meso*-Tetrakis[4-(allyloxy)phenyl]zinc Porphyrin (3).** A mixture of metal-free porphyrin **2** (3 g, 0.0036 mol) and Zn(OAc)$_2$·2H$_2$O (2 g, 0.009 mol) was refluxed in DMF (40 mL) for 20 min. The solution was cooled and poured into cold water, and the solid was filtered, washed with water, and dried. The product was purified by column chromatography over siliga gel (dichloromethane). Yield: 2.9 g (91%). Anal. Calcd for $C_{56}H_{44}N_4O_4Zn$: C, 74.54; H, 4.90; N, 6.21. Found: C, 74.11; H, 4.66; N, 6.38. FT-IR (KBr, cm^{-1}): 3448 (br), 2929 (w), 1656 (s), 1608 (s), 1512 (s), 1463 (w), 1385 (vs), 1342, 1240 (vs), 1180 (s), 1113 (w), 1065 (m), 999 (vs), 933 (m), 806 (m), 727 (w). ^{1}H-NMR (CDCl$_3$): δ 4.83 (m, 8H, C=CH$_2$), 5.64 (m, 8H, OCH$_2$), 6.29 (m, 4H, C=CH), 7.29, 8.26 (dd, 16H, C_6H_4), 8.98 (s, 8H, β-pyrrole). UV−vis (CHCl$_3$, nm): 423, 553, 596.

***meso*-Tetrakis[4-[[(triethoxysilyl)propyl]oxy]phenyl]zinc Porphyrin (1).** In a 50-mL flask equipped with a reflux condenser were placed under nitrogen **3** (1.5 g, 0.0017 mol), triethoxysilane (1.1 g, 0.0068 mol), and dichloromethane (20 mL). Chloroplatinic acid (2.6 mg) was dissolved in 5 mL of dry THF and added dropwise. The reaction mixture was refluxed for 10 h, after which triethoxysilane (0.05 g, 0.0034 mol) and chloroplatinic acid (1.3 mg) were added and reflux was continued for a further 10 h. The solvent was removed in a rotavap, the residue was redissolved in chloroform and filtered over silica gel, and the solvent was evaporated. The product was further purified by dissolving in ethyl acetate and precipitated in hexane to obtain a purple solid. Yield: 1.73 g (67%). Anal. Calcd for $C_{80}H_{108}N_4Si_4O_{16}Zn$: C, 61.61; H, 6.98; N, 3.61. Found: C, 61.12; H, 6.67; N, 3.46. FT-IR (KBr, cm^{-1}): 3447 (br), 2928 (w), 1614 (s), 1512 (s), 1439 (w), 1390 (vs), 1342 (m), 1252 (vs), 1173 (vs), 1107 (w), 1077 (vs), 992 (s), 963 (w), 799 (m), 715 (w). ^{1}H-NMR (CDCl$_3$): δ 1.30 (m, 36H, CH$_2$-Si), 1.39 (t, 36H, OCH$_2$CH$_3$), 3.94 (q, 24H, OCH$_2$CH$_3$), 4.23 (m, 8H, CH$_2$), 4.41 (m, 8H, OCH$_2$), 7.25, 8.09 (dd, 16H, C_6H_4), 8.97 (s, 8H, β-pyrrole). UV−vis (CHCl$_3$, nm): 423 (ϵ = 375 249 mol^{-1} cm^{-1}), 553 (ϵ = 17 181), 595 (ϵ = 7530).

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