

Synthesis and characterization of novel rigid two-photon absorbing polymers[†]

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Two-photon absorbing polymers with alternating fluorenyl units as a π -conjugated bridge and bis-benzothiazole or thiazolothiazole as electron-acceptors were synthesized and characterized by IR, elemental analysis, absorption and fluorescence spectroscopy, and thermogravimetric analysis (TGA). Improvement on the solubility was observed in comparison with their phenyl based analogies. The linear absorption and emission spectra were recorded and high fluorescence quantum yields were found. Relatively large two-photon absorption cross-section per repeat unit (420 GM) were measured under fs-pulsed laser excitation. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

Two-photon absorption (2PA) can be defined as simultaneous absorption of two photons through virtual states in a medium.¹ A remarkable feature of this phenomenon is that the probability of a 2PA process is proportional to the square of the incident intensity. It brings important characteristics for two photon materials technology, i.e. upconverted emission and highly localized excitation, which lead to practical applications including two-photon fluorescence imaging, optical limiting, three-dimensional (3D) data storage, 3D microfabrication, and photodynamic therapy.^{2,3}

The history of 2PA started from 1931 when Goeppert-Mayer predicted the possibility of the 2PA. It was observed experimentally in 1960s owing to the advent of ultrafast high-intensity lasers.⁴ However, it was only until mid-1990s, with the increased availability of high-intensity lasers and the discovery of new chromophores exhibiting very large effective 2PA cross-section values,⁵ the door to the applications in photonics and biophotonics was opened and subsequently it initiated extensive investigations in this area. One of the efforts, which is vital to this area, is the development of efficient 2PA chromophores. Since 1990s, a large number of 2PA chromophores were synthesized and many of them exhibited very large 2PA cross-sections.^{5,6} Among them, the largest 2PA cross-section was achieved by macromolecules.⁷ For small molecules the structure-properties relationships are relative well understood,^{3b,6d,8} such as the 2PA cross-section

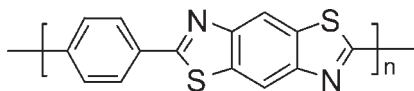
increases with the increase of the conjugation length by facilitation of the delocalization of the electrons. But for the polymers and dendrimers, some issues are still not clear, for example, cooperative effects were observed in polymers or dendrimers with triphenylamino group as donors, shared by two or three conjugated fragments (donor- π -donor).^{7,9} Though these observations were tentatively attributed to the electron transfer along the polymer backbone, more information about polymers with other types of donor or acceptor arrangements will be helpful to understand structure-property relationships. The goal of this article is to evaluate the influence of one of the possible arrangements, i.e. the introduction of an alternative acceptor- π bridge into linear polymers, on the 2PA properties. Benzobisthiazole and thiazolothiazole as π -deficient acceptor groups were selected. It is well known that polymers containing benzobisthiazole, such as poly(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl-1,4-phenylene) (*trans*-PBT) (Scheme 1), have excellent thermal and oxidative stability, good hydrolytic and solvent resistance, high emission quantum yield, and photostability.¹⁰ Others and our previous work also indicated that the benzothiazole group is an efficient electron-acceptor that can lead to high optical non-linearities.^{6e,11} Similarly, thiazolothiazole, which was employed in 2PA chromophores as an electron-acceptor,¹² was also chosen.

Disadvantages of using bisbenzothiazole and thiazolothiazole moieties in polymers, is the rigid-rod nature of these structures, rendering the polymer insoluble in most common solvents. For example, *trans*-PBT can only be dissolved in very strong acid, such as methylsulfonic acid. To compensate for this shortcoming, dialkylated fluorene as a π -conjugated bridge was chosen. Fluorene based chromophores are generally highly fluorescent and strongly conjugated due to the highly delocalized π electrons in the two nearly coplanar

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Scheme 1. Structure of *trans*-PBT.

benzene rings. A series of fluorene based chromophores, synthesized in our laboratory and others, also exhibited large 2PA cross-sections. More importantly, due to the alkyl chains at nine positions extending away from the conjugated π -system, make such derivatives highly soluble in common organic solvents and provide good compatibility with other matrices. The combination of the fluorenyl π -system and the thiazole acceptors is expected to result in polymers that will exhibit both high two-photon absorptivity and good material properties. Herein, the synthesis and characterization of two such polymers are described.

EXPERIMENTAL

General

All the reagents and solvents were purchased from Acros Organics and Aldrich, and used as received unless otherwise mentioned. Tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and dimethylformamide (DMF) were dried using standard procedures.¹³ ¹H- and ¹³C-NMR spectra were recorded on Varian Gemini NMR spectrometer at 300 and 75 MHz, respectively. Elemental analyses were performed by Atlantic Microlab. UV-visible spectrophotometric measurements were recorded on a Varian Cary 3 spectrophotometer at room temperature in 10 mm quartz cuvettes. Steady-state fluorescence was recorded with a PTI Quantmaster spectrofluorimeter using a Xe lamp and excitation monochromator. Thermogravimetric analysis (TGA) measurements were performed with a TA Instruments model TGA 2050 under N₂ at heating rate of 20°C/min.

Synthesis of 9,9-didecylfluorene 5

Fluorene 4 (25 g, 150 mmol) was dissolved in DMSO (80 ml) in a 500 ml three-necked flask, fitted with an addition funnel, two stoppers, N₂ inlet and stirring bar. To the mixture was added powdered KOH (42.06 g, 740 mmol) and KI (1.20 g, 7 mmol), then 1-bromodecane (100 g, 450 mmol) was added via addition funnel over a period of 1.5 hr. The reaction mixture was stirred at room temperature for 18 hr, poured into water, and extracted with CH₂Cl₂. The organic extract was washed with water, dried over MgSO₄, and concentrated. 1-Bromodecane and DMSO were removed by vacuum distillation. The crude product, an orange oil, was purified by column chromatography on silica gel using hexane as eluent, affording 53.5 g of colorless oil (80% yield).¹⁴ ¹H-NMR (300 MHz, CDCl₃): δ 7.68 (d, 2H), 7.29 (d, 6H), 1.95 (bm, 4H), 1.02 (bm, 28H), 0.86 (t, 6H), 0.60 (bs, 4H).

Synthesis of 2,7-dibromo-9,9-didecylfluorene 6

To a solution of 9,9-didecylfluorene 5 (40 g, 89.53 mmol) in propylene carbonate (90 ml) was added *N*-bromosuccinimide (38.24 g, 214.84 mmol) at 60°C in one portion, and the mixture was stirred at 65°C until ¹H-NMR (CDCl₃) data showed the reaction was completed (about 8 hr). The mixture was diluted

with 800 ml of water and extracted in hexane. The organic phase was washed with water, dried and concentrated to give 53.53 g of colorless oil that solidified (99% yield), mp = 36–37°C (lit. mp 38.1–38.9°C).¹⁴ This was used without further purification in the next step. ¹H-NMR (300 MHz, CDCl₃, ppm): δ 7.50 (m, 2H), 7.43 (bm, 4H), 1.91 (m, 4H), 1.18 (bd, 28H), 0.86 (t, 6H), 0.58 (bs, 4H).

Synthesis of 9,9-didecylfluorene-2,7-dicarbaldehyde 7

To a solution of 2,7-dibromo-9,9-didecylfluorene 6 (8 g, 13.23 mmol) in dry THF (80 ml), cooled in a dry ice-acetone bath was added *n*-BuLi (22.0 ml of 1.6 M solution in hexane, 34 mmol) dropwise over 25 min. After 20 min, DMF (3.1 ml, 39.78 mmol) in THF (9 ml) was added and the mixture was stirred in the cooling bath for 2 hr and outside the bath for 4 hr. The reaction mixture was then cooled to 5°C, treated with aqueous HCl (2 ml of concentrated hydrochloric acid diluted with 8 ml water), and diluted with 100 ml of toluene. The combined organic phase was washed with dilute sodium bicarbonate solution and dried over magnesium sulfate. Removal of toluene under reduced pressure afforded a yellow oil. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (90:10) as eluent, affording 5.73 g of white solid (85% yield), mp = 50.5–51.5°C. Anal. Calcd for C₃₅H₅₀O₂ (502.77): C, 83.61%; H, 10.02%; O, 6.36%. Found: C, 83.45%; H, 10.14%. ¹H-NMR (300 MHz, CDCl₃, ppm): δ 10.07 (s, 2H), 7.90 (d, 6H), 2.06 (m, 4H), 1.15 (bd, 28H), 0.83 (t, 6H), 0.56 (bs, 4H). ¹³C-NMR (74.5 MHz, CDCl₃, ppm): δ 192.2, 152.9, 145.7, 136.5, 130.5, 123.5, 121.5, 55.9, 40.4, 32.3, 30.3, 29.9, 29.8, 29.7, 24.3, 23.1, 14.6.

Synthesis of 2,7-bisbenzothiazole-9,9-didecylfluorene 3

A mixture of 9,9-didecylfluorene-2,7-dicarbaldehyde 7 (0.5 g, 0.99 mmol), 2-aminothiophenol (0.3 g, 2.48 mmol), and DMSO (4 ml) was heated at a bath temperature of 195°C for 2.5 hr under N₂, and then poured into water. The separated solids were collected, reslurried in 1:4 acetic acid/water (50 ml), filtered, and washed with water and dilute sodium bicarbonate solution. These solids were purified through a silica gel column using first hexane/EtOAc (90:10), followed by hexane/toluene (70:30) resulting in 0.482 g of yellow solid (68% yield), mp = 79–80.5°C. Anal. Calcd for C₄₇H₅₆N₂S₂ (713.09): C, 79.21%; H, 7.85%; N, 3.92%; S, 8.99%. Found: C, 78.95%; H, 7.82%; N, 3.86%. ¹H-NMR (300 MHz, CDCl₃, ppm): δ 8.12 (q, 6H), 7.93 (d, 2H), 7.85 (d, 2H), 7.50 (t, 2H), 7.40 (t, 2H), 2.16 (bs, 4H), 1.11 (bd, 28H), 0.79 (t, 6H), 0.68 (bs, 4H). ¹³C-NMR (74.5 MHz, CDCl₃): δ 167.9, 153.7, 151.8, 142.5, 134.6, 132.6, 126.8, 126, 124.8, 122.7, 121.3, 121.2, 120.4, 55.7, 40.1, 31.7, 29.8, 29.4, 29.3, 29.1, 23.7, 22.5, 14.

Synthesis of polymer 1

9,9-Didecylfluorene-2,7-dialdehyde 7 (0.15 g, 0.298 mmol) and dithiooxamide (35.9 mg, 0.298 mmol) in 1 ml dry DMF were refluxed for 5 hr under Ar. The product separated from the solution as a sticky oil during the reaction and solidified upon cooling. The solid was collected by suction filtration and washed with CHCl₃ in a Soxhlet extractor for 3 days, affording 0.103 g of polymer 1 as an orange solid (59% yield).

Anal. Calcd. for $C_{37}H_{48}N_2S_2$ (584.92): C, 75.98%; H, 8.27%; N, 4.79%. Found: C, 76.17%; H, 8.64%; N, 4.67%. (Note: the calculated value is based on molecular mass of the repeated unit the contribution of the end groups was neglected.) FT-IR (KBr, cm^{-1}): 3440, 2920, 2850, 1605, 1448, 1212.

Synthesis of polymer 2

Into a three-neck, 100 ml reaction flask were placed 9,9-didecylfluorene-2,7-dicarbaldehyde **7** (0.5 g, 0.99 mmol), 2,5-diamino-1,4-benzenethiol dihydrochloride (0.25 g, 1.04 mmol), and polyphosphoric acid (PPA) (2.6 g). The reaction vessel was fitted with a mechanical stirrer, flushed with nitrogen and then stirred under vacuum for 1 hr, at this moment the reaction mixture turned from white to green. The resulting mixture was then heated at 45°C for 16 hr. During this time the reaction mixture became reddish-black. Subsequently, the reaction mixture was heated at 60°C for 48 hr. The mixture was cooled to room temperature and P_2O_5 (1.32 g) was added. The reaction mixture was then slowly heated to 100°C and stirred for 18 hr, followed by heating to 130°C for another 2 hr; at this stage the solution became highly viscous. The reaction mixture was immediately poured into water, resulting in an orange precipitate. The polymer was neutralized with 20% NH_4OH and washed several times with distilled water. The polymer was dried obtaining 0.51 g of an orange solid (81% yield). The polymer was subjected to Soxhlet extraction with butyl acetate for 4 days. The soluble portion, extracted in butyl acetate, was recrystallized from CH_2Cl_2 -hexane, affording an orange solid. Anal. Calcd for $C_{41}H_{50}N_2S_2$: C, 77.55%; H, 7.94%; N, 4.41%. Found: C, 67.27%; H, 7.95%; N, 4.48%. FT-IR (KBr, cm^{-1}): 3050, 2929, 2851, 1634, 1606.

2PA measurements

The 2PA cross-sections, δ , of the polymers and the model compound were measured using a degenerate two-photon-induced fluorescence (2PF) method. Here a strong tunable pump beam excites the chromophore via 2PA and the total integrated fluorescence is monitored as a function of input frequency. The femtosecond (fs) source used for the pump beam was a fiber ring oscillator, Ti:sapphire based regenerative amplifier laser system (CPA-2001, CLARK-MXR), providing laser pulses at 775 nm of 120 fs duration at a 1 kHz repetition rate. This laser in turn pumps an optical parametric amplifier system (TOPAS, Light Conversion), tunable from 579–950 nm and providing the 10–150 nJ energy range used to produce the 2PF in the materials under investigation. The samples were prepared in CH_2Cl_2 or $CHCl_3$ solutions at concentrations $\sim 1.0 \times 10^{-4}$ M, which were placed within 1.0 cm path length quartz cuvettes. Normally, other solvents would be used for 2PA measurements but the solubility of the polymers precluded use of other solvents.

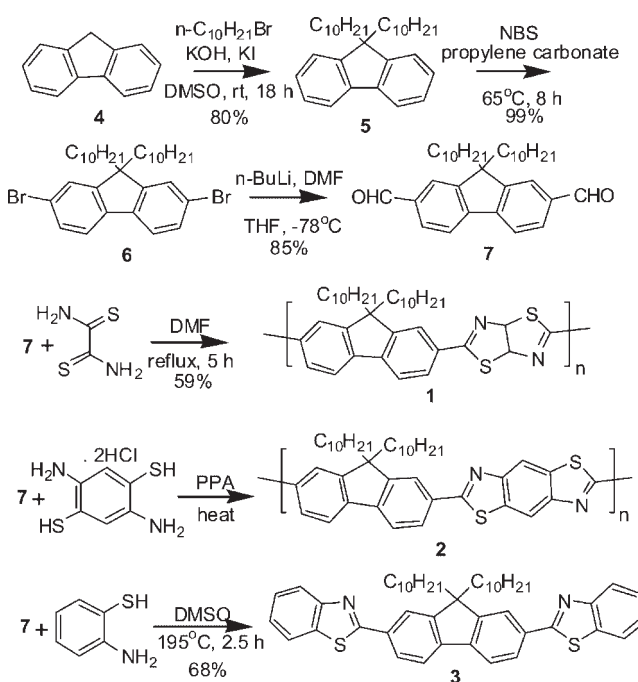
The sample holder compartment was housed within a fully automated spectrofluorimeter (M-6/2003, Photon Technology International). Following excitation of the sample via the strong pump beam, the full two-photon induced fluorescence spectrum was recorded to make certain that the up-converted fluorescence spectrum is independent of pump frequency (not always the case).¹⁵ The spectrum was integrated over the entire emission range to obtain the total integrated fluores-

cence for this particular pump wavelength. Finally, varying the pump wavelength allows one to build up the full 2PA spectrum. 2PF is quadratically dependent on the pump irradiance, therefore it is crucial to correct for irradiance changes with pump wavelength. This can be very time-consuming endeavor and so the fluorescence measurement made is a relative one.¹⁶ The 2PF results obtained for the chromophores under investigation were calibrated against well-know references standard: fluorescein in water (pH 11)¹⁷ and 1,4-bis(2-methylstyryl)benzene in cyclohexane.¹⁸ The collection geometry inside the fluorimeter apparatus was kept constant for all samples.

RESULTS AND DISCUSSION

The polymers were synthesized by condensation of the 2,7-dicarboxaldehyde fluorine derivative **7** with 2,5-diaminobenzene-1,4-dithiol or dithioamide. The key intermediate **7** was prepared from 2,7-dibromo-9,9-didecylfluorene **6** (readily available via bromination of the correspondence dialkylfluorene **5**).^{6c} Similarly, model compound **3** was prepared by reaction of **7** with 2-aminothiophenol in DMF at reflux, and was purified by column chromatography (Scheme 2). Model **3** and the intermediate **7** were characterized by NMR spectroscopy and elemental analysis. The solubility of polymers **1** and **2** presented some limitations on characterization. However, the IR spectra of polymers **1** and **2** reveal that the characteristic carbonyl stretching vibration, present at 1680 cm^{-1} for **7**, disappeared as expected. The combination of the elemental analysis data and dramatic change in the solubility strongly suggests formation of the polymers. In addition, no melting point was observed for polymers **1** and **2**, rather decomposition began at ca. 400°C, confirmed by TGA.

However, in contrast to the totally insoluble *trans*-PBT, it was possible to prepare dilute solutions of both polymers in



Scheme 2. Synthesis of the polymers **1**, **2** and the model compound **3**.

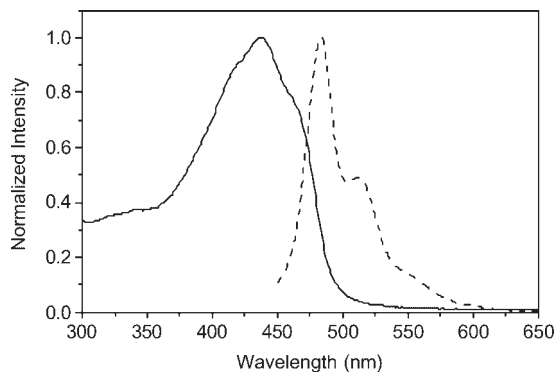


Figure 1. Normalized UV-vis and fluorescence spectra of polymer **1** ($\lambda_{\text{max}}^{\text{abs}} = 438 \text{ nm}$, $\lambda_{\text{max}}^{\text{em}} = 483 \text{ nm}$) in CHCl_3 .

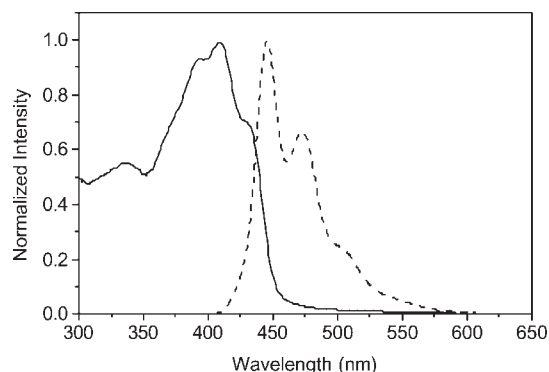


Figure 2. Normalized UV-vis and fluorescence spectra of polymer **2** ($\lambda_{\text{max}}^{\text{abs}} = 409 \text{ nm}$, $\lambda_{\text{max}}^{\text{em}} = 445 \text{ nm}$) in CH_2Cl_2 .

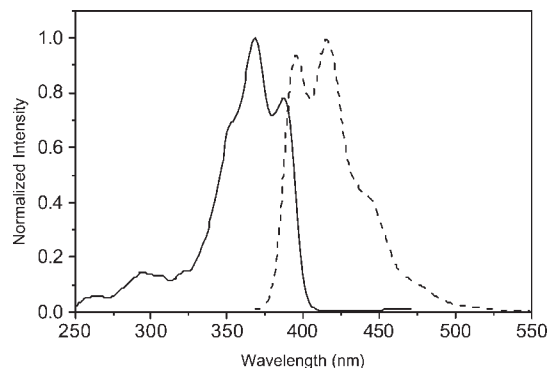


Figure 3. Normalized UV-vis and fluorescence spectra of model compound **3** ($\lambda_{\text{max}}^{\text{abs}} = 369 \text{ nm}$, $\epsilon = 76\,000 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{max}}^{\text{em}} = 415 \text{ nm}$) in CH_2Cl_2 .

halogenated solvents, such as chloroform ($\sim 10^{-4} \text{ M}$ for **1**) or methylene chloride ($\sim 10^{-6} \text{ M}$ for **2**), for absorption and emission measurements. The linear absorption and emission spectra of polymer **1** in CHCl_3 , polymer **2** in CH_2Cl_2 , and the model compound **3** in both solvents are shown in Figs. 1–4. The absorption, emission maxima, and fluorescence quantum yields are summarized in Table 1. A red shift of the absorption was observed for polymer **2** relative to the model compound **3**, commonly observed by the extension of the conjugation length. Polymer **1** exhibited an even larger red shift (69 nm compared to the 40 nm bathochromic shift for polymer **2**). Similar bathochromic shifts were observed in the emission spectra for these polymers, as shown in Figs. 1–4.

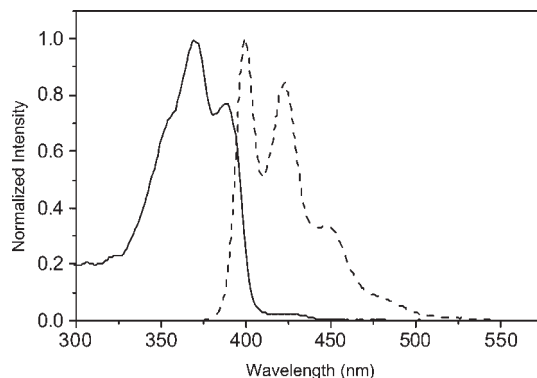


Figure 4. Normalized UV-vis and fluorescence spectra of model compound **3** ($\lambda_{\text{max}}^{\text{abs}} = 370 \text{ nm}$, $\epsilon = 79\,000 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{max}}^{\text{em}} = 400 \text{ nm}$) in CHCl_3 .

Table 1. Absorption and emission data of polymers and the model compound in various solvents

Compound	Solvent	$\lambda_{\text{max ab}}(\text{nm})$	$\lambda_{\text{max em}}(\text{nm})$	ϕ_{fl}
Polymer 1	CHCl_3	438	483	0.58
Polymer 2	CH_2Cl_2	409	445	0.52
Compound 3	CHCl_3	369	415	—
Compound 3	CH_2Cl_2	370	400	0.74

All these materials possessed high fluorescence quantum yield, from 0.58–0.74, making them suitable for using 2PF to estimate their 2PA cross-sections. Quantum yields, ϕ , were calculated from the corrected fluorescence spectra by a standard method,¹⁹ relative to Rhodamine 6G in ethanol ($\phi \approx 0.94$).²⁰

The measurement of the 2PA cross-sections was done according to a previously reported procedure.²¹ The concentration of the repeat units was estimated according to the extinction coefficient of the model compound (**3**) in the same solvent. (Note: it was not possible to estimate the number of the repeat units for polymer **2** since its poor solubility prohibited the gel permeation chromatograph (GPC) or viscosity measurement. The effort of measuring molecular mass by MALDI-TOF technique on going.) Figure 5 shows the quadratic dependence of the intensity of 2PF on the incident (excitation) laser power, confirming that the observed fluorescence was indeed a result of two-photon

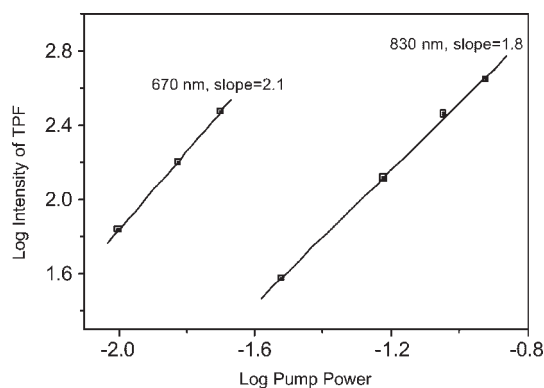


Figure 5. Two-photon fluorescence quadratic behavior of polymer **1** in CHCl_3 .

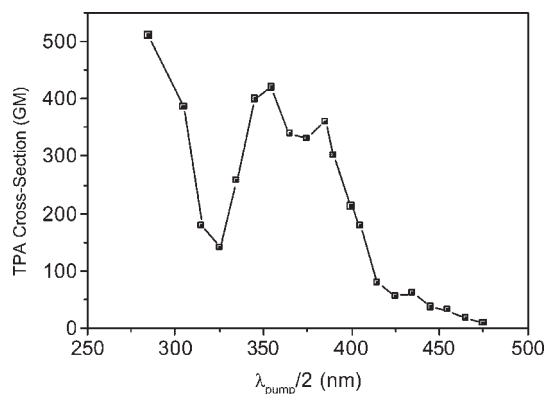


Figure 6. Estimated 2PA cross-section per repeat unit for polymer **1** in CHCl_3 . $\text{GM} = 10^{-50} \text{ cm}^4 \text{ sec/photon}$.

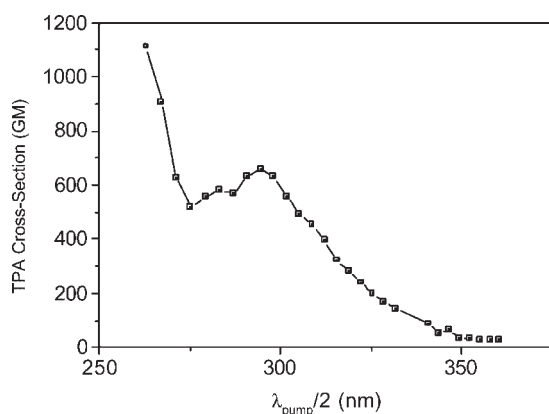


Figure 7. 2PA cross-section of model compound **3** in CH_2Cl_2 .

excitation. The 2PA cross-sections of polymer **1** and compound **3** are shown in Figs. 6 and 7, respectively. The 2PA cross-sections are plotted versus the sum of the energies of the two photons involved in the degenerate process (this energy has been converted to wavelength for reference). The 2PA cross-section for polymer **2** was not determined due to its limited solubility (the concentration was too low to obtain accurate data). The 2PA cross-section of polymer **1** at 710 nm is 420 GM, lower than that of the model compound **3** (660 GM at 588 nm); where $\text{GM} = 10^{-50} \text{ cm}^4 \text{ sec/photon}$. This is likely due to aggregation of the polymer chains induced by strong π - π interactions.

CONCLUSIONS

Conjugated polymers with alternating thiazole electron-accepting and fluorenyl π -conjugated bridge moieties and a model compound were synthesized and characterized. Polymer **1** exhibited a large fluorescence quantum yield and relatively high 2PA cross-section per repeat unit. A further increase in the 2PA cross-section may be realized if aggregation of polymer **1** can be circumvented. Replacement of the primary alkyl groups by branched alkyl chains, such as 2-ethylhexyl groups at nine positions of the fluorene bridge, could increase the solubility and dramatically reduce the π - π stack interaction, a matter of current investigation.²²

The good chemical, thermal, and photochemical²³ stability, combined with desirable one- and two-photon absorption and luminescence properties, makes these rigid-rod type polymers particularly promising materials for two-photon based technologies.

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