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Thiophene Dendrimers as Entangled Photon Sensor Materials

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Abstract: The ability to do spectroscopy with a small number of entangled photons is an important development in the area of materials and sensing. This report investigates the effects of increasing thiophene dendrimer generation on the cross-section for both entangled (σ_E) and random (δ_E) two-photon absorption cross-sections. Nonlinear optical properties of dendrimers are an interesting area of study because of potential applications in optical signal processing and remote sensing, and the use of a nonlinear optical material as a sensor for entangled photons offers great possibilities for applications in quantum lithography. Entangled two-photon absorption (ETPA) experiments and two-photon excited fluorescence (TPEF) experiments vary by at least 10 orders of magnitude in the photon flux used to probe the material. ETPA cross-sections from liquid samples as well as those of thin-film samples are investigated. An increase in σ_E and δ_R with increasing dendrimer generation is observed, suggesting that the thiophene groups within the dendrimer nonlinearly absorb in a cooperative manner, which is further evidenced in the variation of cross-section per thiophene group. The nonlinear spectroscopic features obtained by the TPEF measurements were also obtained by the ETPA experiments, despite the fact that 10 orders of magnitude fewer photons are used in the latter technique. All dendrimer generations investigated in this work are found to have great potential for applications in quantum optical devices.

I. Introduction

Organic conjugated macromolecules have been the subject of intense study for applications such as organic light-emitting diodes,[1−5] photovoltaic devices,[6] light harvesting,[7−12] molecular electronics,[13,14] and optical signal processing.[15−18] Among the many methods of tailoring organic molecules for these applications, chromophores designed in dendritic architectures have been shown[5,10,12,14,19−21] to hold great promise, as dendrimers exhibit efficient intramolecular energy transfer and energy migration, leading to enhanced nonlinear optical (NLO) properties relative to those of the monomeric architecture. One unexplored application of NLO materials is in detection of entangled photon pairs generated by spontaneous parametric downconversion (SPDC).

The intensity-dependent random nonlinear effect related to the excitation of virtual intermediate states is traditionally explored through two-photon excited fluorescence (TPEF) spectroscopy.[22] In TPEF spectroscopy, the rate of two-photon absorption (TPA) is proportional to the product of the probability of being in the virtual or real intermediate state and the rate of excitation from that intermediate state to the excited state. Since each of these quantities depends linearly on input flux, the TPA rate has a quadratic dependence on input flux. As TPEF relies

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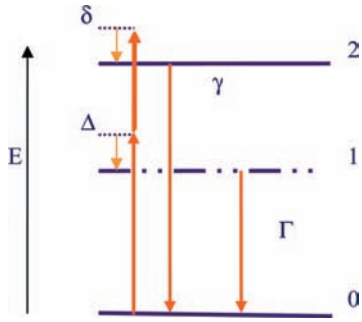

Figure 1. Simplified three-level energy diagram of a molecule, with 0, 1, and 2 denoting the ground state, intermediate, and two-photon excited state, respectively. The detuning energy and population decay rate for the excited state are represented by δ and γ, while those of the virtual state are Δ and Γ. Within this diagram, the virtual state 1 is not accessible by a one-photon excitation.

on random absorption events, a potentially damaging flux of over 10^{20} photons cm^{-2} s^{-1} incident on the sample is required to generate the measurable fluorescence photon count rate necessary to determine a random TPA cross-section. Decreasing the flux necessary to observe the NLO effect would allow extended time measurement in microscopy applications, such as the imaging of biological materials.

Unlike TPEF, which relies on classical photons, correlated photon pairs generated by SPDC are used in entangled two-photon absorption (ETPA) experiments. Photon pairs produced by SPDC have a high degree of temporal and spatial correlation. This is critical for demonstrating a relatively efficient TPA event.[23] While traditional TPEF spectroscopy relies on a two-step absorption, ETPA is a process in which the transition is accomplished in a single step through the coherent superposition of the ground and excited states: the first photon of the entangled pair promotes the molecule to a virtual intermediate state, and the second photon, within the virtual state lifetime, completes the excitation.[23] As such, the ETPA process, illustrated in Figure 1, is expected to depend not only on the detuning energy and the differences between the photon energy and the virtual- and excited-state energies, but also on the entanglement time T_E, which is the time delay between the photons within the entangled pair. As one might expect, the ETPA cross-section of a molecule is known[24,25] to contain a term inversely proportional to T_E, reflecting the fact that the probability of both photons within the pair arriving within the virtual-state lifetime can be increased by decreasing the delay between the photons. However, the ETPA cross-section is also expected[24,25,27] to have a non-monotonic variation with T_E; constructive and destructive interference between the entangled photons can occur. Reports in the literature have theorized[24,25] and demonstrated[27] the possibility of performing virtual state spectroscopy using entangled photons by adjustment of the entanglement time T_E. Through this non-monotonic variation of the ETPA cross-section with T_E, the virtual-state energy level can be determined.[24,25,27] This molecular property cannot be measured using classical photons. From a molecular perspective, the ETPA cross-section depends not only on the transition matrix elements, but also on the detuning energy for the intermediate and excited states, as well as the entanglement time.

Theoretical investigations by multiple research groups have shown[23−26] that the ETPA rate should have a linear rather than quadratic dependence on the intensity of downconverted light. However, experimental demonstrations have been limited.[27] Theoretical estimates of the ETPA cross-sections of hydrogen[24] and sodium[25] are reported as 10^{-12} and 10^{-30} cm^2, respectively. Results from ETPA experiments on a free-standing third-generation porphyrin dendrimer film, tetraphenylporphyrin within a polyvinylbutyral matrix, were recently reported.[27] It was found[27] that the ETPA cross-section for a porphyrin dendrimer film was on the order of 10^{-17} cm^2, which is only an order of magnitude lower than the single-photon absorption (SPA) cross-section of 10^{-16} cm^2 at the linear optical absorption maximum of the dendrimer. Furthermore, a transition from linear (entangled) to quadratic (random) absorption rates with increasing input flux density was observed in these experiments far from any resonances of the porphyrin dendrimer. While these initial results have suggested the possibility of using entangled photons for nonlinear spectroscopy, there has not been a systematic demonstration of the use of entangled photons for this purpose reported in the literature.

In this contribution, a set of thiophene dendrimers (Figure 2) synthesized according to reported procedures[28] are systematically investigated as sensors for entangled photons, and the effects of increasing dendrimer generation on the TPA cross-section of these thiophene dendrimers are observed. Previous work on thiophene dend*rons*, essentially half the dend*rimer* we investigate in this report, has shown[20] interesting nonlinear absorption properties. A non-monotonic increase in TPA cross-section of these dendrons was observed,[20] suggesting a cooperative enhancement due to intramolecular interactions between the thiophene branches. While the overall TPA cross-section is found to increase with dendron generation, the TPA cross-section per thiophene unit is found[20] to increase non-monotonically with dendron generation only until the second generation (G2), suggesting a cooperative enhancement of the TPA cross-section. The decrease in TPA cross-section per thiophene in the G3 dendron was attributed[20] to a saturation effect. Here, the TPA cross-section of thiophene dendrimers is investigated through ETPA as well as traditional TPEF experiments. This is the first report of a comparison between trends in the TPA cross-sections measured by these techniques in a systematic manner for a complete set of dendrimers varying in generation. In addition, thin-film as well as liquid samples are investigated and compared in this work to determine if either medium is more effective as a sensor for entangled photons.

II. Experimental Section

A. Materials. The thiophene dendrimers investigated in this work were synthesized by an iterative divergent/convergent method starting from a trimethylsilyl (TMS)-protected branched terthiophene.[28] A solvent of tetrahydrofuran (THF, Sigma-Aldrich, 99.9% purity) was used for thiophene dendrimer liquid samples. The optical density for the solutions prepared was controlled by concentration. Concentrations used for TPEF and ETPA experiments are reported in Tables 1 and 2, respectively, in the Results and Discussion section.

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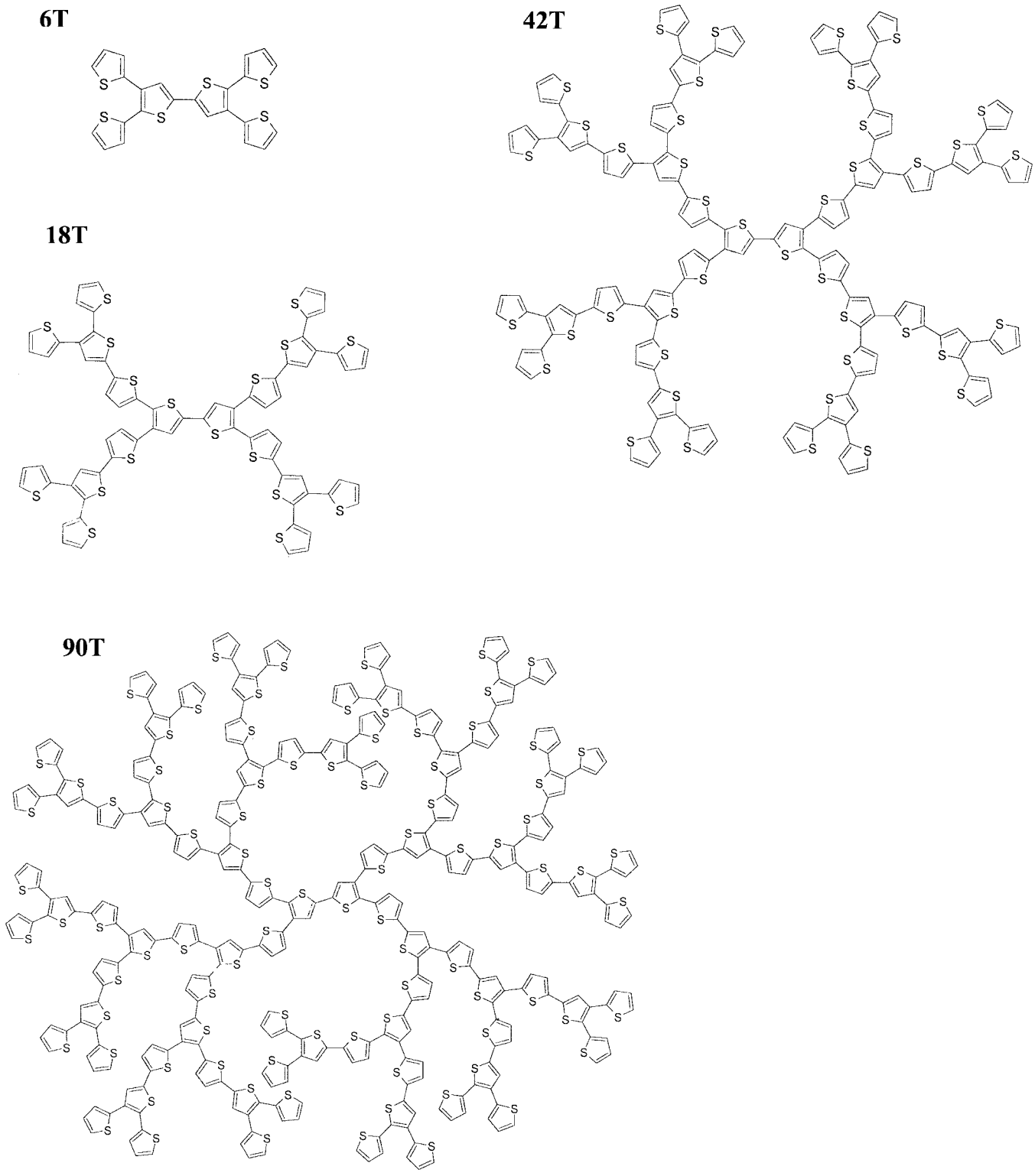

Figure 2. Thiophene dendrimers **6T** (top left), **18T** (middle left), **42T** (top right), and **90T** (bottom). Dendrimers are named according to the number of the thiophene groups.

Thin-film samples were drop-cast in poly(ethyl methacrylate-*co*-methyl acrylate) (PEMA-MA, Aldrich, $M_w \approx 10^6$ g/mol) with solvent tetrahydrofuran (THF, Aldrich, spectrograde, inhibitor free) onto a glass substrate. Film thickness and uniformity were assessed using a Dektak surface analyzer. All films studied were prepared to have a uniform thickness between 10 and 80 μm, varied by dendrimer generation to yield a reasonable single-photon absorption spectrum, which matches steady-state spectra in liquid samples and hence shows that there is no aggregation of the thiophene dendrimers within the film. Dendrimer concentrations, as obtained from number density, are reported in Table 2.

Steady-state absorption experiments were performed using an Agilent 8341 UV/vis spectrometer, and fluorescence measurements with a Jobin Yvon-SPEX Fluoromax-2 spectrometer.

B. Two-Photon Excited Fluorescence. The TPEF method[22] was employed to evaluate the random TPA cross-sections (δ_R) of the liquid samples. The random TPA cross-section δ_R was evaluated over the excitation wavelength range of 700−850 nm using a mode-

Table 1. Results from Steady-State Linear Absorption and Two-Photon Excited Fluorescence Measurements

		steady-state			two-photon excited fluorescence at 800 nm	
no. of thiophenes in dendrimer	sample concentration (μM)	λ_{abs} (nm)	λ_{em} (nm)	Φ_{fl}	random TPA (δ_R) (GM)	δ_R/thiophene (GM)
6	12	382	483	0.11	6	1.0
18	10	384	548	0.08	230	12.8
42	8.5	387	570	0.07	620	14.8
90	7.0	389	596	0.04	1130	12.6

Table 2. Entangled Two-Photon Absorption Cross-Sections

			ETPA cross-section, σ_E			
	dendrimer concn (μM)		absolute (cm^2 molecule^{-1})		relative to **90T**	
no. of thiophenes in dendrimer	liquid	film[a]	liquid, $\times 10^{-18}$	film, $\times 10^{-17}$	liquid	film
6	360	2800	0.13	0.33	0.1	0.22
18	115	1200	0.71	0.98	0.26	0.32
42	52	250	2.6	2.0	0.67	0.74
90	36	250	5.9	3.7	1	1

[a] Concentration obtained from number density.

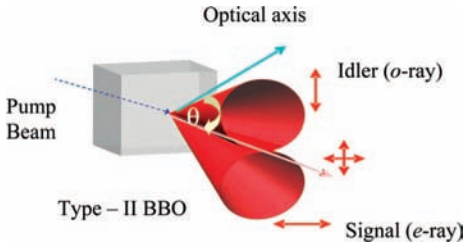

Figure 3. Illustration of collinear phase-matching condition of type II SPDC. Idler (vertical polarization) and signal (horizontal polarization) "cones" of photons are overlapped along one line.

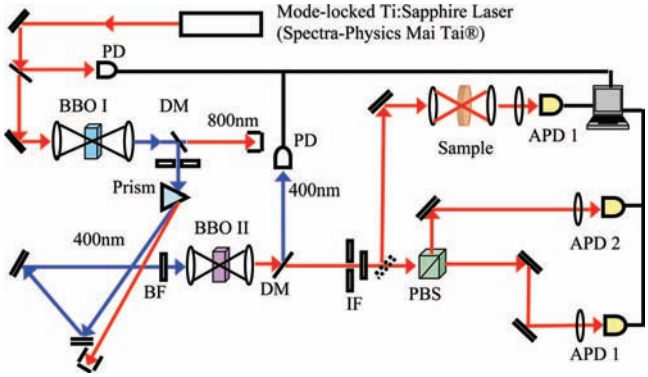

Figure 4. Experimental setup for ETPA experiments. Dichroic mirrors (DM) are used to separate second-harmonic from fundamental, and entangled photons from second-harmonic. Switching to analysis/coincidence counting requires addition/removal of one mirror between the interference filter (IF) and polarization beamsplitter (PBS). Photodetectors (PD) are used as a reference for fundamental and second-harmonic power, while avalanche photodiode (APD) single-photon counting modules detect entangled photons.

locked Ti:sapphire laser (Spectra-Physics MaiTai HP, pulse width <100 fs, 80 MHz repetition rate). In the TPEF technique, TPA cross-sections were measured relative to a reference solution of 10^{-4} M Coumarin 307 in methanol.

C. Entangled Two-Photon Absorption. Our system is designed such that entangled pairs of photons are generated at a wavelength of 800 nm through the SPDC of photons at 400 nm wavelength under the collinear phase-matching conditions illustrated in Figure 3. Within the SPDC process, momentum and energy are conserved within each photon pair. The experimental setup is illustrated in Figure 4. Briefly, sub-100 fs pulses, typically 14 nm fwhm centered at 800 nm with an 82 MHz repetition rate, from a mode-locked Ti:sapphire laser (Spectra-Physics MaiTai) are frequency-doubled to produce a second-harmonic generation (SHG) beam at 400 nm. This SHG beam is then focused onto a 0.5 mm thickness β-barium borate (BBO II in Figure 4) crystal designed for type II SPDC to generate entangled pairs of downconverted photons. Within type II SPDC, signal (o-ray) and idler (e-ray) photons are generated at orthogonal polarization.

Down converted photons are detected by silicon avalanche photodiode (APD) single-photon counting modules (Perkin-Elmer SPCM-AQR-13). Using these APDs individually, the single-photon count rate at a given detector is measured. A Glan-Taylor polarization beamsplitter is used to direct the idler and the signal to separate APDs to allow concidence counting by a fast coincidence counting module (Ortec NIM7400, 10 ns coincidence window) connected to the two APDs. With this setup, maximum input photon rates of $\sim 3 \times 10^7$ photons/s for the singles count rate and 2.2×10^5 photons/s for the coincidence count rate are obtained. To vary the input flux, the fundamental beam is attenuated using a continuously variable neutral density filter wheel, with photodetectors serving as references for the input power. ETPA measurements are performed based on the transmission method, with appropriate corrections for background and scatter. Film samples are oriented perpendicular to the incoming SPDC pump, with the film centered at the focal point of the sample telescope. The experimental setup and method used for these experiments have previously been demonstrated[27] effective for ETPA measurements.

III. Results and Discussion

A. Linear Optical Spectroscopy. Results from steady-state absorption and fluorescence are illustrated in Figure 5. From these absorption spectra, a red-shift of the absorption maximum and a broadening on the red side of the peak are observed with increasing number of thiophenes. These effects have been observed in thiophene dendrons and ascribed[20,29] to absorption by α-thiophene chains of different lengths within the dendron. The absorption spectrum of the dendron is produced by a linear combination of absorption spectra from individual α-thiophene

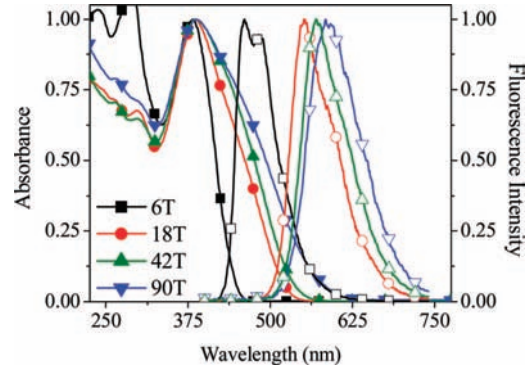

Figure 5. Normalized absorbance (closed symbols, left axis) and emission (open symbols, right axis) spectra for thiophene dendrimers. Absorbance and emission maxima are red-shifted with increasing dendrimer generation.

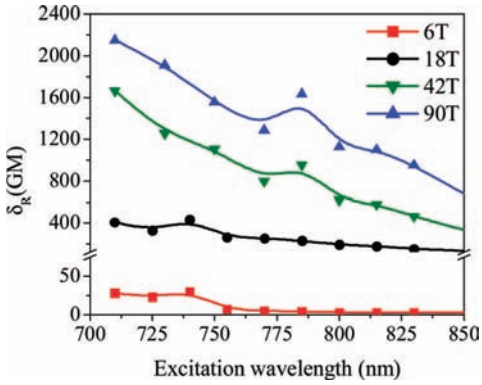

Figure 6. Two-photon absorption cross-section, δ_R, for thiophene dendrimers plotted against excitation wavelength.

chains.[20,29] A red-shift of emission maximum with increasing number of thiophenes is observed in the thiophene dendrimers studied in this work. Previous work on thiophene dendrons has shown[20,29] that this shift in emission maximum can be attributed to emission from the longest α-thiophene chain. With linear spectroscopy alone, the delocalization of excitation and absorption within these dendrimers cannot be explicitly evaluated; a complementary set of nonlinear TPA measurements is necessary to evaluate delocalization within these dendrimers.

Fluorescence quantum yield Φ_{fl} (Table 1) is calculated by a known method[30] using Coumarin 307 as a standard. The quantum yield is found to decrease with dendrimer generation. Based on previous studies of thiophene dendrons[20] through time-correlated single-photon counting methods, this decrease in quantum yield may be a result of an increase in nonradiative decay rate, through intersystem crossing to a non-emissive state, with increasing dendrimer generation.

B. Two-Photon Excited Fluorescence Spectroscopy. The TPA cross-sections were estimated using the TPEF method.[22] Fluorescence was collected for each dendrimer at the emission maximum determined from steady-state spectroscopy (Figure 5, Table 1). TPA cross-sections of the various dendrimers as a function of excitation wavelength are shown in Figure 6. A pronounced increase in cross-section with increasing dendrimer generation is observed. At an excitation wavelength of 800 nm, TPA cross-sections for the dendrimers are found to increase from 6 GM to ~1100 GM (1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}) as the dendrimer generation increases, a trend which has been attributed to delocalization of the excitation over the entire dendrimer.[20,31] The TPA cross-section of the **42T** dendrimer in this work is found to be nearly identical to that of the **45T** dendron previously reported.[20] Comparing the thiophene dendrimers in this work to nitrogen-centered phenylacetylene dendrimers previously reported,[32] the thiophene dendrimer is found to yield a larger TPA cross-section than the phenylacetylene dendrimer does for a given dendrimer generation. Recently, thiophene macrocycles have been reported[31,33] to have TPA cross-sections of 10^4-10^5 GM, with TPA cross-sections per thiophene group of 10^2-10^3 GM. The thiophene dendrimers reported here are found to have a smaller TPA cross-section per subgroup than the macrocycles do. However, the dendrimer architecture may have greater potential in energy transport applications due to the ability of branch-core systems to funnel energy.[21]

Thus, the main spectroscopic trends are that the TPA cross-section increases with increasing dendrimer generation and number of thiophene units, and that the TPA cross-section per thiophene is found to be at a maximum for the **42T** dendrimer. While a larger TPA cross-section is observed in the **90T** dendrimer than in the **42T** dendrimer, a smaller TPA cross-section per thiophene is found. These trends have been explained[20,31] through time-resolved measurements for the case of dendrons by a cooperative enhancement of the TPA cross-section through an increase in branching, with a saturation effect occurring in the highest dendrimer generation.

C. Entangled Two-Photon Absorption Measurements. The ETPA rate,[34] R_E, is derived from time-dependent second-order perturbation theory in terms of the second-order correlation function.[35] Theoretically, the ETPA effect is accompanied by non-entangled or random TPA effect.[23] From this, a bimodal distribution is observed in the flux-dependence of the absorbed photon rate. At low input photon flux density, the ETPA rate dominates and the observed absorption rate is demonstrated[24,25,27] as linear with input flux. From this, the overall TPA rate R_E is expressed as the summation of the linear ETPA rate and the quadratic, random TPA rate:[24,25,27]

$$R_E = \sigma_E \phi + \delta_R \phi^2 \quad (1)$$

where σ_E is the ETPA cross-section, δ_R is the random TPA cross-section, and ϕ is the input photon flux density of photon pairs. The critical flux ϕ_{crit} is defined[24,25] as the flux at which the linear and nonlinear absorption rates are equal. ϕ_{crit} is calculated as

$$\phi_{crit} = \frac{\sigma_E}{\delta_R} \quad (2)$$

Below ϕ_{crit}, the absorption of entangled photons is expected[24,25] to dominate over random TPA, enabling a clear evaluation of the ETPA cross-section.

There exist two factors critical in an ETPA process: the entanglement time T_E, and the entanglement area A_E. The entanglement area is determined by the angular width of the fourth-order coherence function[24] and depends on the pump beam waist, the pump beam wavefront, and the crystal length. It has been shown that the entanglement area can be increased by decreasing the interaction length of the SPDC process, as well as by decreasing the spot size of the SPDC pattern through focusing.[36] The entanglement area is related[24,25,27] to the entangled and random TPA cross-sections and the entanglement time by

$$A_E = \frac{\delta_R}{2\sigma_E T_E} \quad (3)$$

where the entanglement time T_E is equivalent to the difference between the transit times of the correlated photon pair through

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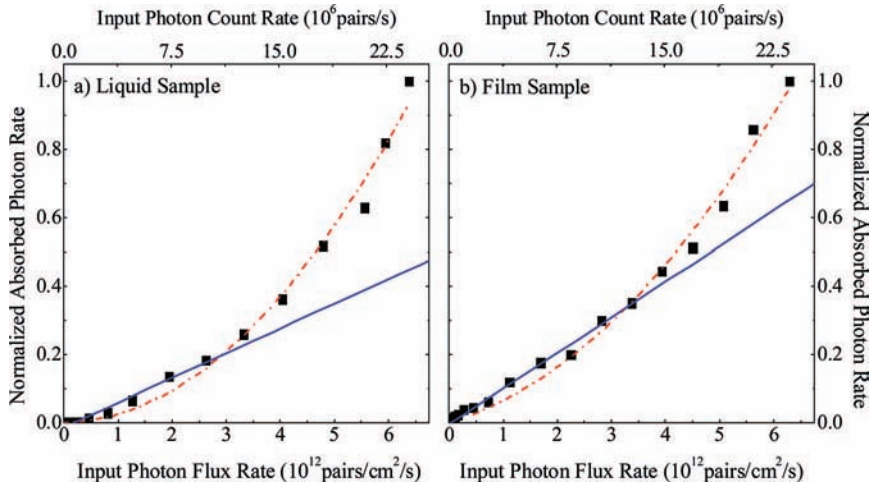

Figure 7. Normalized absorbed photon rate for **90T** dendrimer/THF liquid samples (a) and **90T** dendrimer film sample (b) plotted against input flux (bottom axis) and photon count rate (top axis). The linear component of the absorbed photon rate is shown with a solid blue line, while the quadratic component is shown with a dashed red line.

the nonlinear crystal.[37] It has been theorized[24,25] and demonstrated experimentally[27] that virtual-state spectroscopy can be performed through the variation of the entanglement time; through measurement of the ETPA cross-section as a function of entanglement time, the energy of the virtual states of a molecule can be obtained.

An interference filter was employed to obtain a SPDC pump wavelength of 800 nm for these ETPA experiments. Entangled two-photon absorption is observed in all generations of dendrimer investigated in this work. Shown in Figure 7 is the plot of normalized absorbed photon rate against input photon flux for the **90T** dendrimer prepared in solution and in thin film. Both linear and quadratic character are observed, which, from eq 1, is due to ETPA and random TPA, respectively. From these plots, it is shown that ETPA for these thiophene dendrimers is measurable with an input flux on the order of 10^{12} photons cm^{-2} s^{-1} in both types of samples.

ETPA cross-sections were extracted from the linear component of the absorption and are summarized in Table 2. These ETPA cross-sections are on the order of 10^{-18} cm^2 molecule^{-1} for liquid samples and 10^{-17} cm^2 molecule^{-1} for film samples. The ETPA cross-sections are nearly on the order of single-photon absorption cross-sections of these dendrimers. The magnitude of these ETPA cross-sections compares well to that obtained from ETPA experiments performed[27] on porphyrin dendrimers. A linear dependence of ETPA cross-section on generation is observed in these thiophene dendrimers, as seen in other reports of thiophene macrocycles[31,33] and *dendrons.*[20] From this, ETPA experiments are found to be sensitive to the cooperative interaction of the thiophene units within the dendrimers. The single-step, two-photon ETPA process appears to be probing the same spectral property of the molecule that the two-step random TPA process does. For a given film sample, σ_E is 5−25 times that of the corresponding liquid sample. It is found that the ratio $\sigma_{E,film}/\sigma_{E,liquid}$ decreases exponentially with the number of thiophenes in the dendrimer. The dendrimer films were prepared such that the number density of chromophores was on the order of 10^{20} molecules/cm^3, 1 or 2 orders of magnitude greater than that of equivalent liquid samples, so there may be a greater degree of intermolecular coupling in the thin-film sample than in the liquid sample.

A higher-order nonlinear absorption (HoNLA) cross-section on the order of 10^{-30} cm^4 s photon^{-1} (10^{20} GM) was determined from the quadratic component of the absorbed photon rate. Although the possibility of random TPA is suggested by eq 1, the incredible difference in order of magnitude between this HoNLA cross-section and the random TPA cross-section obtained from TPEF experiments makes the underlying cause of this uncertain. The HoNLA cross-section is found to increase with dendrimer generation while being independent of sample type. The dependence of the HoNLA cross-sections on the number of thiophene units is found to be nearly identical to that observed in both TPEF and ETPA cross-sections. While this HoNLA cross-section has not been proven in this study to be a result of random TPA of these thiophene dendrimers, the HoNLA cross-section follows the same trend as that of ETPA cross-sections, as well as that of random TPA from TPEF experiments. Based on this result, it is suggested that this nonlinear absorption is due to non-entangled, but nonclassical, photons generated by the SPDC process.

The entanglement time was calculated from the difference in transit times between signal and idler photons produced by the down-conversion crystal.[38] In this experimental setup, T_E is determined to be 96 fs. Using this entanglement time and the results from the ETPA measurements, an entanglement area was calculated from eq 3. Entanglement areas of 4 cm^2 for liquid samples and 0.6 cm^2 for film samples are obtained, and A_E does not appear to vary by dendrimer generation within a given sample type. Several factors may contribute to these macroscopic results for A_E. First, under focused pumping conditions, the divergence of the pump beam used for SPDC contributes to the uncertainty in the entanglement area. As this experiment relies on a mode-locked source rather than a continuous-wave source, creation of correlated photons is expected[39] to be localized rather than random, which may contribute to a further increase in entanglement area over that calculated on the basis of continuous-wave sources.[24] A larger entanglement area is observed in thiophene dendrimers than in previous experimental investigations[27] of porphyrin dendrimers, in which an A_E on the order of 10^{-2} cm^2 was observed. In the case of thiophene

(37) Sergienko, A. V.; Shih, Y. H.; Rubin, M. H. *J. Opt. Soc. Am. B-Opt. Phys.* **1995**, *12*, 859–862.

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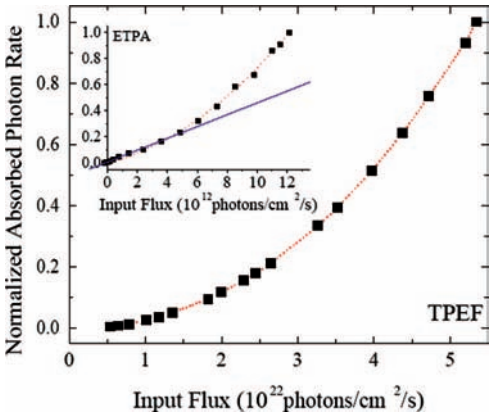

Figure 8. Normalized absorbed photon rate for **42T** liquid samples plotted against input flux rate for ETPA experiments (squares, inset) and traditional TPEF experiments (squares). Solid blue and dashed red lines denote fits of the data to linear and quadratic functions, respectively. Note that the TPEF *x*-axis has units 10^{22} photons cm^{-2} s^{-1}, while the inset ETPA *x*-axis has units 10^{12} photons cm^{-2} s^{-1}.

dendrimers, which are known to be space-filling structures,[28] there may be additional effects from the cooperative interaction between the thiophene units. Previous results for thiophene *dendrons* have shown[20] that excitation is delocalized across the entire dendrimer. A_E is known[24] to have implications in the critical flux ϕ_{crit}. Using eqs 2 and 3, it is found that ϕ_{crit} is inversely proportional to A_E, suggesting that a large A_E allows evaluation of both entangled and random TPA at low input flux. While the ETPA cross-section is also shown[24] to be inversely proportional to A_E, the negative effect of a large entanglement area on σ_E can be compensated for by decreasing the entanglement time T_E by decreasing the delay between signal and idler photons through the addition of quartz plates. An earlier report has shown[27] that σ_E varies non-monotonically with T_E; entangled two-photon transparency can be induced through variation of T_E, which allows additional control over the NLO properties of the material.

For comparison to traditional methods, the absorption rates of **42T** liquid samples against the input flux density for both TPEF and ETPA experiments are plotted in Figure 8. Results from traditional TPEF experiments are shown to be perfectly quadratic. Both linear and quadratic terms, suggesting entangled and random TPA, respectively, are observed in ETPA results. From this, the nonlinear TPA of these thiophene dendrimers can be detected through ETPA measurements using 10 orders of magnitude fewer photons than that necessary for TPEF measurements.

Two-photon absorption cross-sections of the dendrimers, relative to that of **90T**, are plotted in Figure 9 against the number of thiophene units. The relative ETPA cross-sections obtained for dendrimer samples are found to match the trends obtained by TPEF measurements on dendrimers presented in this report, as well as previously published TPEF results for thiophene dendrons.[20] The fact that random TPA trends have been reproduced with ETPA measurements gives additional confidence in the ETPA method. From the results presented in Figure 9, it is shown that nonlinear absorption, and, more importantly, trends in nonlinear absorption cross-section, can be observed by entangled photon pairs using a very low flux.

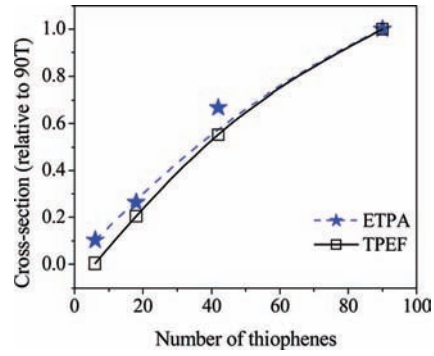

Figure 9. ETPA (stars) and random TPA (open squares) cross-sections relative to those of **90T** for dendrimer liquid samples. Random TPA cross-sections are obtained from traditional TPEF experiments.

IV. Summary

Thiophene dendrimers systematically explored in this work are demonstrated to be effective sensors for entangled photons at very low flux, which has applications in imaging of biological systems and remote sensing as well as quantum optical applications. A linear dependence on input flux, which is a signature of entangled two-photon absorption, is observed in ETPA measurements for all thiophene dendrimers in this study. ETPA effects are observed regardless of whether the sample is prepared as a thin film or liquid. ETPA cross-sections of these dendrimers are measured to be on the order of $10^{-19}-10^{-17}$ cm^2, only one or two orders of magnitude smaller than their linear optical absorption cross-sections. The ETPA cross-sections are found to be an order of magnitude greater in the thin-film samples than in the liquid samples, suggesting that the dendrimer thin films exhibit better performance than dendrimer solutions as detectors for entangled photons. This enhancement due to sample medium is found to be most pronounced in the lower generation dendrimers, where concentration and number density are the highest. Despite differences in the sample medium, nearly identical nonlinear absorption cross-section dependence on the number of the thiophene units in the dendrimer is obtained. Trends in nonlinear absorption cross-section measured by ETPA are found to match those measured by TPEF experiments, despite the fact that 10 orders of magnitude *fewer* photons are used in the ETPA measurements. These results indicate that the ETPA technique probes the same spectroscopic properties that TPEF measurements do. The ability to measure nonlinear optical properties of materials with a very low flux of photons has extraordinary implications in nonlinear spectroscopy and quantum optical applications. Furthermore, our results suggest that the NLO materials explored in this work act as coincidence counters: there is only a two-photon absorption when there is a high degree of temporal correlation (or entanglement) between the photons.

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