Multiphoton Fluorescence Quenching of Conjugated Polymers for TNT Detection

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The use of conjugated organic compounds in fluorescence sensing applications has been demonstrated to provide an impressive method to detect energetic nitro-aromatic compounds. The amplified fluorescence quenching in conjugated polymers was used for trace detection of nitro-aromatics. This method, under one-photon excitation, possesses certain limitations such as the use of harmful ultra-violet radiation and relatively high background noise from light scattering. A novel approach that utilizes the additional benefits of nonlinear optical methods involves multiphoton excited fluorescence. This technique employs infrared excitation which is essential for eye-safety applications and allows for deeper penetration through the atmosphere, with relatively low background noise. We herein report, two conjugated polymers which show good multiphoton absorption properties. This is combined with the excellent sensitivity of the multiphoton excited fluorescence to the presence of tri-nitro toluene (TNT). The multiphoton absorption cross-sections are provided and the Stern−Volmer plots are discussed. This technique, in combination with the great analyte sensitivity of various organic materials, promises to be an important sensing technology in the infrared spectral regions.

Introduction

Conjugated polymers have proven very useful in creating highly sensitive fluorescent chemical and biological sensors.[1−5] The ability of these polymers to give amplified responses is attributed to the efficient electron delocalization and migration of excitons over relatively large distances.[1] The use of amplified sensing polymers provides several advantages derived from the ability to synthetically tailor these materials to a required resonance energy, solubility, and even chemical selectivity for particular applications.[5−10] One can enhance the utilization of these materials by combining these desired characteristics with a nonlinear optical probe. In particular, multiphoton excitation[11−16] of these systems may potentially provide additional selectivity and for the case of fluorescence applications the use of the second and third order input intensity dependence by the emitted fluorescence reduces the background noise from the excitation in a sensing scheme and allows one to move out of the visible excitation regime (excitation can be in the near-IR and beyond). This approach can greatly improve safety issues by means of working as a remote sensing method, which also eliminates the use of harmful UV light radiation. Therefore, the utilization of two photon and three-photon excited fluorescence of amplifying fluorescent organic materials in the IR range with fs pulse lasers is very attractive for the detection of improvised explosive devices at a safe stand-off distance.

In this report, we show that two- and three-photon excitation of these amplifying fluorescence polymers can be applied for the detection of 2,4,6-trinitrotoluene (TNT). The polymers under investigation are **P1** and **P2**, shown below in Figure 1. It is found that these systems have large two-photon cross-sections and the multiphoton emission is sensitive to the presence of TNT.

The complete synthesis and characterization of the two polymers used in this study were reported previously.[5−7,17,18] Previous studies have shown that **P2** is a very efficient chemosensory structure for the detection of TNT.[6−8] The pentiptycene units in this polymer provide photoluminescence stability and high solid-state quantum yields.[5−7] In effect, the three-dimensional, noncompliant iptycene structures isolate the polymer backbones of **P1** and **P2** and thereby reduce intermolecular electron/orbital coupling and the self-quenching that usually accompanies these interactions.[5−10] Both polymers have absorption bands near ∼400 nm which is attributed to a π to π^* transition in the conjugated backbone structure.

Experimental Methods

Multiphoton Excited Fluorescence Measurements The multiphoton excited fluorescence measurements were carried out as follows. The laser used for two photon excited fluorescence (2PEF) was a Kapteyn Murnane (KM) mode-locked Ti:sapphire laser with a repetition rate of 76 MHz and pulse width of 35 fs. The average power was in the range of 0−10 mW. The wavelength was set at 800 nm. For the three- photon excited fluorescence (3PEF), the light beam from an optical parametric amplifier (OPA) was used with 100 fs pulses at a wavelength of ∼1300 nm with a repetition rate of 1 kHz. The maximum

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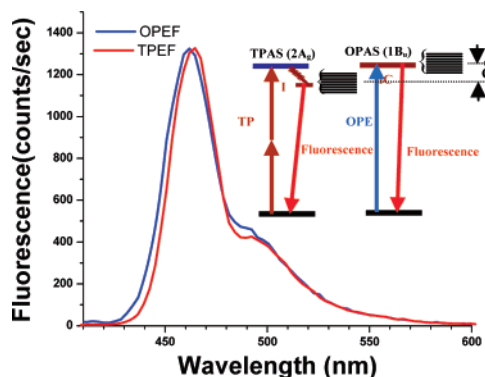[‡] Massachusetts Institute of Technology.
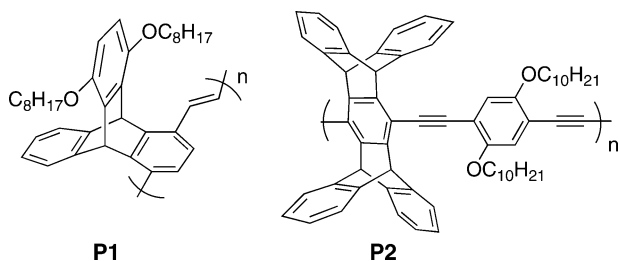
Figure 1. Investigated polymers **P1** and **P2** with three-dimensional iptycene units isolating the polymer backbone.

Figure 2. One and two photon-excited fluorescence spectra for **P2**, showing the inhomogenous broadening of the polymer.

TABLE 1: Linear and Nonlinear Optical Properties of the Investigated Molecules

| sample	abs. (nm)	linear em. (nm)	2PA em. (nm)	quantum yield	δ (GM) 800 nm
P1	413	470	477	0.76	44980
P2	426	454	460	0.35	2332

a δ values reported here are for entire chain (**P1**, $M_n = 7.9 \times 10^5$ g/mol, **P2**, $M_n = 3.7 \times 10^4$ g/mol). Experimental error ±5%.

average power in this experiment did not exceed 1 mW. A logarithmic plot between the collected fluorescence photons and input intensity gave a slope of two/three, ensuring quadratic/cubic dependence between the same, for two/three photon emission measurements. From a known procedure,[13] the two photon absorption cross section, δ_{2PA}, was determined. Similarly, the three photon absorption cross section, δ_{3PA}, was also determined by following a known method.[15] For this purpose, the one photon excited fluorescence (1PEF) measurements were performed by using fourth harmonic of the idler of the OPA, and the data from the experiment was used to calculate the three photon absorption cross-section.

Multiphoton Fluorescence Quenching Experiment. Fluorescence quenching experiments were carried out by microtitration in solution. The multiphoton-excited fluorescence quenching was performed as follows. Initially, the 2PEF spectrum was recorded in the absence of quencher at room temperature and measurement of the 1PEF spectrum following subsequently. For the 2PEF quenching, we used the same laser and optical parameters that were used to measure the two photon absorption cross-sections, whereas the 1PEF quenching was performed using the Fluoromax-2 (SPEX) spectrophotometer. To the initial solution were performed microliter additions of a solution that contained the polymer at the same concentration and the quencher at a known concentration, and the 1PEF and 2PEF spectra were repeatedly acquired after each microliter addition. The 3PEF spectra were also acquired in the same manner as described above, except that it was recorded separately, using the fourth harmonic of the idler of the OPA. Stern−Volmer plots were made with the acquired data.

Results and Discussion

For a comparison, measurements of the one-photon fluorescence quenching by TNT of **P1** and **P2** was performed. We obtained quenching responses of similar magnitude (in terms of their Stern−Volmer plots) as those previously reported.[17−19] As shown in Figure 2, the one and two photon emission spectra are nearly the same. This is in agreement with previous reports obtained for other polymers,[20,21] suggesting that the final relaxed (emitting) states are similar with either excitation method. The small but reproducible shift of ∼3 nm in the emission spectrum (Figure 2) excited via TPA process with respect to that excited via the one photon absorption process energy has been detected using exactly the same detection configuration in both cases and by inserting the second harmonic unit with an IR-rejecting filter for one photon excitation. This shift can be explained by the inhomogeneous broadening in the polymer. Due to the internal conversion from a two-photon allowed state ($2A_g$) to a one-photon allowed fluorescent state ($1B_u$), the TPA process populates a slightly different (lower energy) group of energy levels of the inhomogeneous system of the polymer. This is shown in the inset of Figure 2. The fluorescence line shift with excitation energy for one-photon excitation was previously

documented for polymers.[22] In spite of the small shift in the emission spectra due to inhomogeneity of the relaxed fluorescence electronic state, the emitting state corresponds to the same electronic transition for both modes of excitation.

Two-photon excited fluorescence determinations were made with fs pulses in the near-IR (∼760 to 840 nm). Measurements of the intensity dependence of the multiphoton emission on the input photon intensity allowed for the first estimates of the two photon absorption (TPA) cross-sections in these systems.

From these measurements it was found that the cross-sections were large with ∼45,000 GM for **P1** and ∼2300 GM for **P2** (per entire chain). These two polymers have different chain lengths which result in close values of δ (normalized per repeat unit). Specifically, this number near the two-photon absorption maximum for **P2** is 54 GM (at 800 nm), whereas for **P1** it is 51 GM at 765 nm (see Table 1). These values are of the same order of magnitude when compared with previous TPA cross-section measurements with poly(phenylene vinylenes).[23] It is well-known that the conjugation length of the organic molecular structure can have a significant impact on the two-photon absorption properties.[16,24] A power law dependence (4−7) of the nonlinear optical properties on the length of polymer chains has been predicted.[20,24] One can expect enhancement in the TPA cross-section in polymers as compared to their respective monomers by virtue of strong intramolecular interactions.[25−28]

It is important to note that the two important issues here are the large two-photon cross-sections per gram/mol and the ability to synthesize high molecular weight polymers with high quantum yields and long-range exciton migration that will allow a large dynamic range of sensitivity. The desired property is the maximum two-photon fluorescence, and this can be accomplished either by synthesizing good two-photon building blocks for the amplified polymers or by increasing the number of strongly coupled building blocks (conjugation length). It appears that with these two polymers both approaches can be realized. The three-photon absorption cross section (δ_{3PA}) was determined[15] from the described experimental method and was found to be $11.16 \pm 10 \times 10^{-79}$ cm^6 s^2; similar numbers have been observed in large macromolecular systems possessing cooperative enhancement of nonlinear response.[15,29] The utilization

Letters

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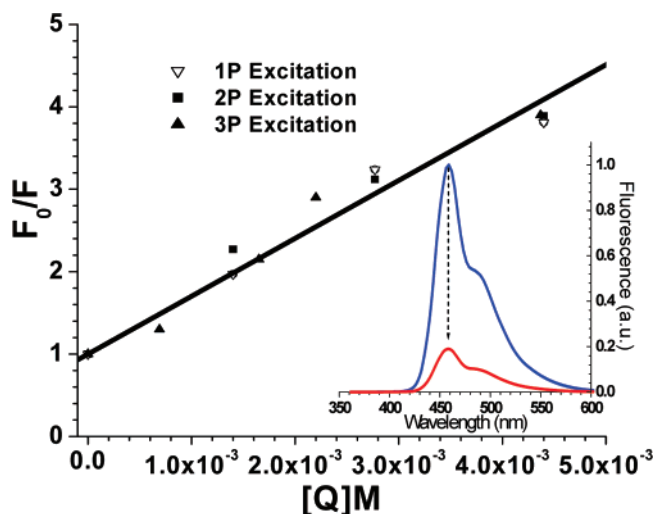
Figure 3. Stern−Volmer plots for one and two photon. Inset: Quenching factor of 5 times observed from the spectra at milli-molar concentrations of TNT.

of the three-photon excited fluorescence allows one to move to the IR, specifically into the transparency window for the atmosphere which is advantageous for remote sensing. Also, the determination of the three photon absorption cross section and its wavelength dependence in conjugated polymers can yield important information about the various intrinsic molecular details, not accessible by the traditional spectroscopic methods.

The iptycene units in **P1** and **P2** prevent dense packing of the polymer chains and increase the permeability thereby increasing the response of the material to analytes such as TNT.[5−7] The Stern−Volmer plot for polymer **P2** obtained via two-photon excitation at 800 nm and via three photon excitation at 1300 nm is shown in Figure 3. The quenching effects in **P1** were also investigated. Here, it was found that the quenching factor was only ~1.2 at 5×10^{-3} M TNT which is significantly lower than that found for **P2**. This again demonstrates the good transport properties of **P2** which may be due to the rigid structure of the polymer. The mechanism of the quenching observed via multiphoton excitation was examined by Stern−Volmer analysis and a linear dependence on the analyte (TNT) concentration was found. Previous studies on similar conjugated polymeric systems have shown that the one-photon excited fluorescence quenching by nitro-aromatics is usually dominated by static quenching.[9,10,19]

The mechanism for the quenching process observed in **P2** may involve charge-transfer complexes that are formed between the analyte's nitro-aromatic electron acceptors and the electron rich polymer chain. The Stern−Volmer quenching constant K_{SV} estimated from the Stern−Volmer plot was 0.73×10^3 M^{-1} and is in qualitative agreement with previous measurements performed in solutions using one-photon excitation for similar polymers.[17−19]

The one-photon (linear) excitation quenching is also shown for comparison. A quenching factor of ~5 at 5×10^{-3} M TNT, was observed for either modes of excitation. This indicates that the quenching is associated with the same relaxed emitting state. Although it is the case for this polymeric system, it is not certain that all materials will behave in the same way under one, two, and three-photon excitation. In fact, differences between the relaxation routes for two-photon and one-photon excitations observed by Frolov et al.[30] may provide an additional control that can potentially lead to additional analyte selectivity. It is well-known that the one- and three-photon excitation, regardless

of molecular symmetry, obey the same parity selection rules,[15] as opposed to that for two-photon excitation. Therefore, using three-photon excitation, we can directly populate the same electronic state as for one photon excitation. However, when compared with one and also two photon excitation, we can use even longer excitation wavelengths for three photon absorption-based applications which provides deeper penetration depths in scattering or absorbing media. This affords the polymers the ability to sense TNT in the IR wavelengths with fs pulses at a relatively lower background noise and also for reasons of eye safety.

Conclusions

In conclusion, we have performed multiphoton absorption measurements in two amplified sensing polymers, using infrared excitation. The polymers display large two-photon absorption cross sections, and their bright multiphoton excited fluorescence is sensitive to the presence of TNT. We performed two-photon and three-photon excited fluorescence quenching measurements in the presence of TNT. The two and three- photon excited fluorescence quenching of **P2** was large (quenching factor ~5 at millimolar concentrations). The ability to carry out multiphoton excited fluorescence quenching measurements offers several advantages for sensitive detection in the IR spectral regions, and the use of femtosecond pulses (with low average power) may offer an advantage for applications concerned with eye safety. Further enhancement of the two-photon absorption cross-section may be carried out by synthetic modifications based on known structure−function relationships. The development of such polymers as multiphoton sensors with controlled properties may offer a new avenue for selective chemical detection systems.

Supporting Information Available: Other experimental details are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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