

Optically Excited Entangled States in Organic Molecules Illuminate the Dark

L. Upton,^{†,‡} M. Harpham,^{‡,||} O. Suzer,^{†,||} M. Richter,[§] S. Mukamel,[§] and T. Goodson, III^{*,†,‡}

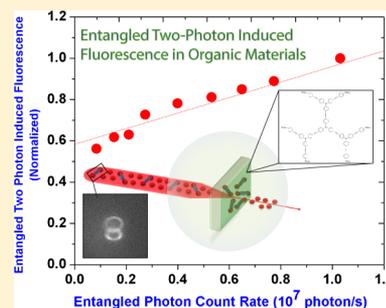
[†]Applied Physics and [‡]The Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, United States

[§]The Department of Chemistry, University of California, Irvine, California 92697-2025, United States

S Supporting Information

ABSTRACT: We utilize quantum entangled photons to carry out nonlinear optical spectroscopy in organic molecules with an extremely small number of photons. For the first time, fluorescence is reported as a result of entangled photon absorption in organic nonlinear optical molecules. Selectivity of the entangled photon absorption process is also observed and a theoretical model of this process is provided. Through these experiments and theoretical modeling it is found that while some molecules may not have strong classical nonlinear optical properties due to their excitation pathways; these same excitation pathways may enhance the entangled photon processes. It is found that the opposite is also true. Some materials with weak classical nonlinear optical effects may exhibit strong non-classical nonlinear optical effects. Our entangled photon fluorescence results provide the first steps in realizing and demonstrating the viability of entangled two-photon microscopy, remote sensing, and optical communications.

SECTION: Spectroscopy, Photochemistry, and Excited States



Quantum entanglement¹ has surprisingly proven to have implications in numerous physical applications. For example, it is a critical ingredient for the fast transfer of information as well as the encryption of data.² Optically, it is responsible for elusive quantum communication protocols and nonlocality representation schemes.^{3,4} Quantum entanglement has been discussed in such diverse fields as biology to computer system's logic.^{5–8} It is found that sometimes the details of quantum mechanics give rise to phenomena that might be counterintuitive to our classical driven sense of reason. A number of studies have analyzed the effects of decoherence within quantum systems⁹ and the feasibility of generating entanglement schemes for long-distance quantum communication.¹⁰

We present findings of fluorescence as a result of quantum-entangled two-photon excitation in an organic material. These measurements take advantage of the nearly 10 orders of magnitude enhancement observed when entangled (versus classical) two-photon measurements are carried out.^{11–13} This is a major step toward the ability to selectively detect small emission signals resulting from a nonlinear process. In general, a large flux is needed to observe emission from two-photon absorption,¹¹ yet we demonstrate that when using entangled photons it is possible to carry out two-photon excited fluorescence with a small input flux 10¹⁰ photons/cm²s compared with 10¹⁸ photons/cm²s. This approach may be implemented in a number of quantum optical sensors and detectors. The measurable enhancement despite lower input flux is useful when one considers the potential damage biological samples may incur when probed with the high flux fields needed for multiphoton fluorescence microscopy.¹⁴

Along with results of emission from an entangled source, we also discuss the entangled two-photon absorption and fluorescence electronic state mechanisms that govern the interactions between the entangled photon states and electronic material states. With such mechanisms, it will be possible to predict entanglement sensitive molecules, thus allowing us to design molecules optimized for particular quantum processes and applications. This report offers what could be the first step toward real applications of quantum entanglement in the detection and manipulation of electronic states in organic (biological) materials.

Classical two-photon absorption (TPA) is a third-order nonlinear optical process.¹⁵ It is an extremely inefficient process¹⁶ requiring a very high input flux of photons to overcome the small cross sections. To increase the two-photon probability, high-peak-intensity pulsed lasers are generally utilized. One can get a sense of the inefficiency of this process by comparing the two-photon absorption cross section (TPACS) to the one-photon absorption cross section. Cross sections for two-photon absorption in most organic chromophores are typically on the order of 1 × 10⁻⁴⁸ cm⁴s/photon. The one-photon cross section is, in general, on the order of 1 × 10⁻¹⁶ cm².

To describe these nonlinear interactions between light and matter, it is useful to invoke higher order optical coherence theory. Classical TPA can be described with second-order correlation functions.¹⁷ It then follows that the rate for classical

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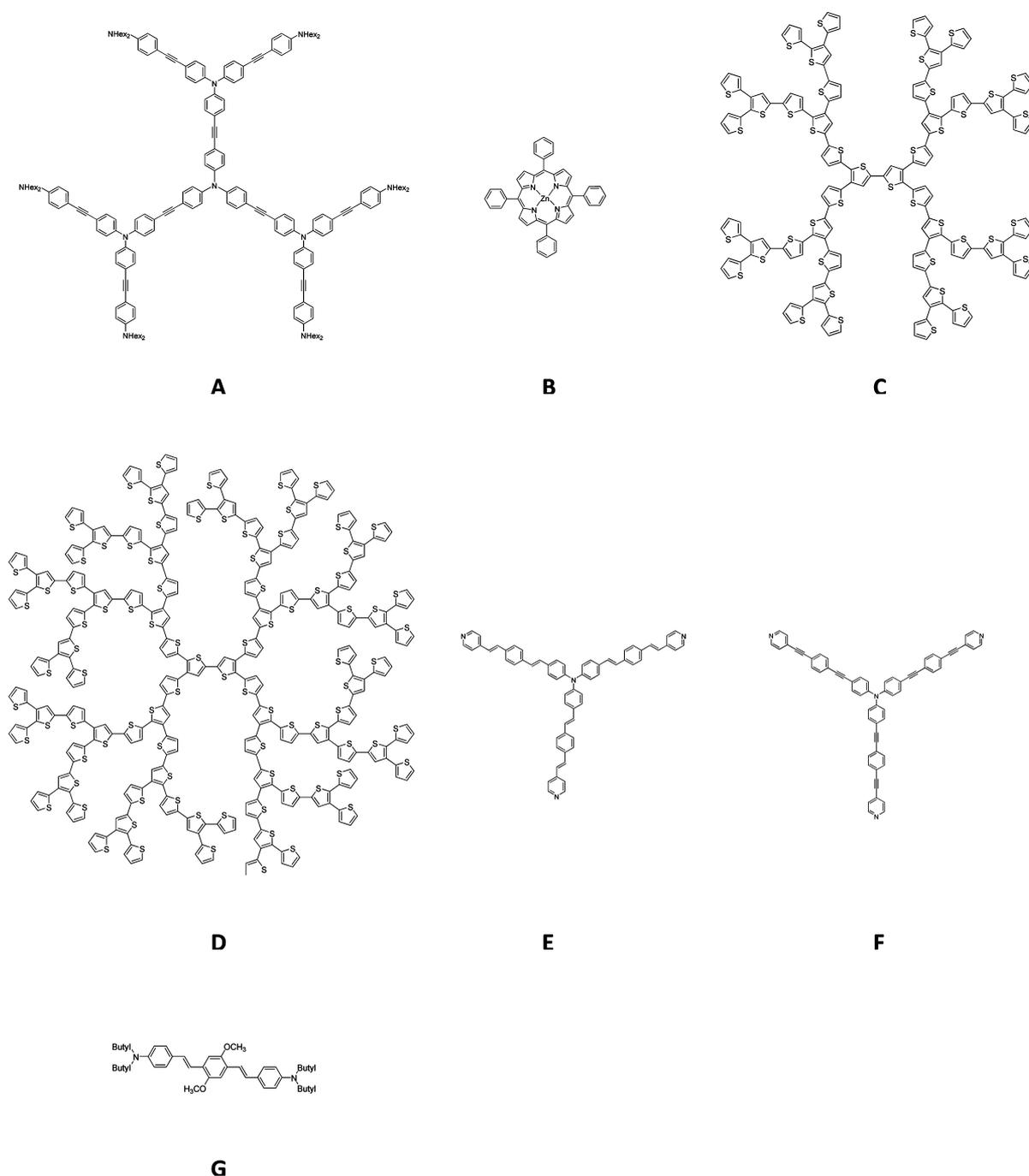


Figure 1. Structures and labeling scheme for compounds studied in this paper.

two-photon processes is quadratic in nature. Unlike single-photon absorption there is a (ϕ^2) dependence on the fields. Using second-order perturbation theory, the classical two-photon absorption cross section (TPACS) δ_R is given¹⁶ by:

$$\delta_R = \frac{\pi}{2} \omega_1^0 \omega_2^0 \delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0) \times \left| \sum_j \left[\frac{D_j}{\Delta_j^{(1)} - i\kappa_j/2} + \frac{D_j}{\Delta_j^{(2)} - i\kappa_j/2} \right] \right|^2 \quad (1)$$

where ω_1^0 and ω_2^0 are the frequencies of the of the two photons, $\delta(\varepsilon_f - \varepsilon_i - \omega_1^0 - \omega_2^0)$ enforces conservation of energy, ε_f and ε_i are the energy eigenvalues of the ground and excited state,

respectively, $D_j = \langle \psi_f | e \cdot \mu | \psi_j \rangle \langle \psi_j | e \cdot \mu | \psi_i \rangle$ give the transition dipole matrix elements between the ground and excited states, κ_j are the state linewidths, and $\Delta_j^{(k)} = \varepsilon_j - \varepsilon_i - \omega_k^0$ is the energy mismatch, and $k = 1$ or 2 refers to each of the photons involved in the interaction. In organic systems, the size of the cross section can be manipulated by increasing the conjugation length in the molecule and by utilizing different donor–acceptor configurations.^{18,19} It should be noted that two-photon absorption can occur in molecules via a permanent dipole transition or via a virtual state transition.²⁰

Moving beyond the classical regime of nonlinear optics to study the effects of quantum-correlated photons in nonlinear spectroscopy, we see that the quantum effects caused by entangling the excitation source vary the interaction mechanism

between the fields and the material system and provide a method of probing the quantum pathways of these material systems.²¹ Entangling the source also provides more flexibility and control of bandwidth and temporal resolution than classical sources,²² yet the effects of these correlations between the entangled photon states on material electronic states have not yet been fully characterized. Not only is the cross section modified but also the two-photon processes are no longer quadratic in intensity dependence. To fully describe the interactions between entangled photon pairs and matter it is again useful to consider higher order optical coherence theory. Entangled photons generated by the process of spontaneous parametric down-conversion have a high level of spatial and temporal correlation described by fourth-order correlation functions.²³ Because the photons are correlated, the absorption rate has linear intensity dependence instead of the normal quadratic dependence for two-photon absorption, despite it also being a two-photon process. The entangled two-photon cross section σ_e is given as:²⁴

$$\sigma_e = \frac{2\pi}{(\hbar\epsilon_0 c)^2 A_e T_e} \omega_i \omega_s \delta(\epsilon_f - \epsilon_i - \omega_i - \omega_s) \times \left| \sum_j \left\{ D_{is}^{(j)} \frac{1 - \exp[-iT_e \Delta_j^{(i)}]}{\Delta_j^{(i)}} + D_{si}^{(j)} \frac{1 - \exp[-iT_e \Delta_j^{(s)}]}{\Delta_j^{(s)}} \right\} \right|^2 \quad (2)$$

where \hbar is Planck's constant, ϵ_0 is vacuum permittivity, c is the speed of light, A_e and T_e are entanglement area and entanglement time, respectively, ω_i and ω_s are the frequencies of the idler and signal photons, $\delta(\epsilon_f - \epsilon_i - \omega_i - \omega_s)$ enforces energy conservation, ϵ_f and ϵ_i are the energy eigenvalues of the ground and excited states, respectively, $D_{is}^{(j)} = \langle \psi_i | e_i; \mu | \psi_f \rangle \langle \psi_i | e_s; \mu | \psi_f \rangle$ gives the transition dipole matrix elements, and $\Delta_j^{(k)} = \epsilon_j - \epsilon_i - \omega_k$ is the detuning energy where $k = i$ or s refers to the signal and idler photons. The fourth-order correlation functions pertaining to the fields are contained within the spatial and temporal contributions of A_e and T_e . It is also important to note that unlike the classical TPACS, the entangled cross section is inversely proportional to A_e and T_e .

Theory states that the ETPA rate is not an exclusive process consisting only of the entangled photon cross section times the flux density of photon pairs ($\sigma_e \phi$) but is accompanied by a nonentangled or random TPA effect²⁵ involving two non-correlated photons. The entangled two-photon absorption rate, R_E , is derived²⁶ in the same manner as eqs 1 and 2 using time-dependent second-order perturbation theory to determine the cross sections and using correlation functions to determine the flux dependence.¹⁷ The overall TPA rate with contributions from both entangled and classical two-photon absorption R_E is thus expressed^{11,13,27} as the sum of the linear ETPA rate and the quadratic, random TPA rate. The overall TPA rate is given by

$$R_E = \sigma_e \phi + \delta_R \phi^2 \quad (3)$$

where σ_e is the ETPA cross section (eq 2), δ_R is the random TPA cross section (eq 1), and ϕ is the input photon flux density of photon pairs. For small input flux, the entangled contribution dominates. However, as flux increases the random TPA rate takes over.

Using an entangled photon experimental protocol provided in the Supporting Information, we excited several classes of molecules at 800 nm, which is far from their single photon resonance energies. We demonstrate that with the use quantum entangled photons and with organic two-photon materials it is

possible to observe relatively bright emission from the absorption of a very small number of entangled photons. Second, we demonstrate that entangled photons are sensitive to the absorption mechanism of the molecule being probed. Lastly, we present a model that describes the mechanism of absorption of entangled photons for various material systems.

While the absorption of entangled photons is interesting for its fundamental implications, the detection of the fluorescence is essential for many technical applications.^{28,29} We measured the entangled two-photon excited-state fluorescence using a method in which the intensity of the entangled photon source is varied and the change in fluorescence intensity is measured. As eq 3 suggests, at small input fluxes the fluorescence should be linearly dependent on the flux of the spontaneously parametric down converted light. Molecules A–D (Figure 1) were used in our absorption and fluorescence studies because of their ability to absorb entangled photons¹¹ and their relatively high fluorescent quantum yields. Steady-state data are provided in the Supporting Information. It must be noted that molecule B does not have a large fluorescent quantum yield and showed no fluorescence. Fluorescence and absorption (direct transmission) measurements were taken simultaneously.

It should be noted from the outset that there are several issues in detecting fluorescence from entangled pairs. Carrying out measurements utilizing a very small input flux is extremely delicate and tedious. Detecting fluorescence from entangled photon excitation above the instrument noise and environmental background is not trivial. The standard fluorescence collection procedure was modified to increase the collection efficiency. A custom fluorescence collection assembly unit is used to increase the fluorescence collection efficiency to ~23% by focusing the fluorescent photons onto our CCD array. When measuring the entangled two-photon fluorescence intensity the total image intensity is averaged over a specified number of pixels (from a CCD camera (Princeton Inst.)).

Shown in Figure 2A is the detectable emission in the tolane dendrimer system, molecule A, as a result of excitation by a very small number of excitation entangled photons. The total collected fluorescence averaged over the CCD array is linearly dependent on input entangled-photon count rate, but unlike the TPA measurements we do not see the quadratic contribution at higher fluxes. It must be noted that the input photons count rate is smaller than the count rate normally required for these nonlinear experiments. The observation of classical two-photon absorption typically requires on the order of 10^{20} photons/second. However, with the use of entangled photons we are able to detect entangled two-photon excited fluorescence with an input photon flux (only 10^7 photons/second). This is the first report of fluorescence in a real material as a result of excitation by entangled photons. This important result implies that the possibility of using entangled photons for real applications in imaging, communication, and in sensing is real. Indeed, the very small flux needed for this nonlinear optical process suggests a nonclassical enhancement in the fluorescent signal.

From our entangled photon absorption measurements an enhanced cross section was obtained for the resulting fluorescent molecule, and this result is shown in Figure 2B. The data for the absorbed photon rate were found to follow closely that predicted by eq 3. Also, experiments of entangled photon absorption were carried out for molecular systems depicted in Figure 1A–D. The entangled photon absorption process found in these systems also suggests that a nonclassical

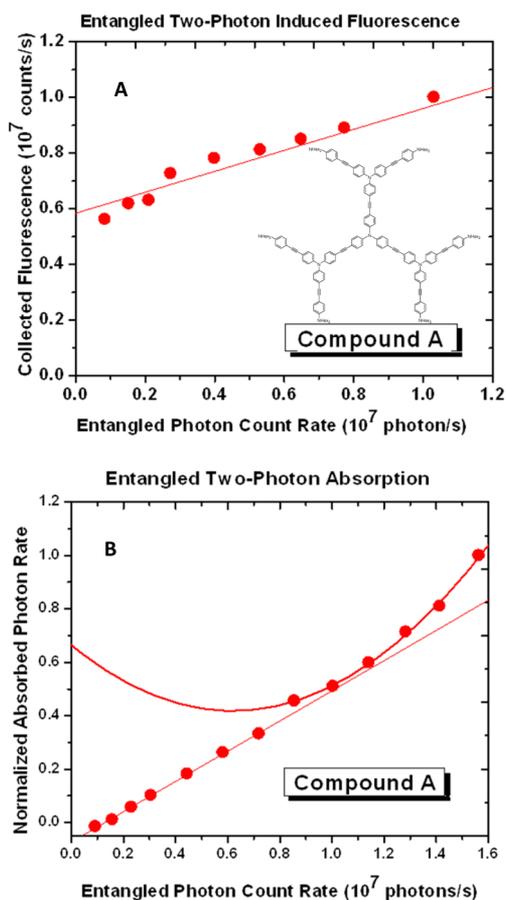


Figure 2. Entangled two-photon excited fluorescence and entangled two-photon absorption of molecule A, a nitrogen-centered tolane dendrimer, are given in (A) and (B). The absorbed photon rate is normalized with respect to the total absorbed photon rate, which is on the order of 10^7 photons/s.

enhancement effect is operative. Interestingly, it is found that entangled photon absorption cross section does not scale with material in the same manner as the classical TPA cross section. As one can see in Table 1, for example, molecule B, which has a

Table 1. Two-Photon Absorption Cross Sections and Entangled Two-Photon Cross Sections

material	TPA cross section ^a	ETPA cross section
	δ_R (GM)	σ_e (10^{-17} cm ²)
(A) first-generation dendrimer	370	2.33
(B) tetraphenylporphine, zinc	20	2.37
(C) 42T thiophene dendrimer	620	1.27
(D) 90T thiophene dendrimer	1130	2.08
(E) T161B	280	no ETPA
(F) T161D	1040	no ETPA
(G) stilbene derivative I	300	no ETPA

^aTPA cross section reported for an 800 nm excitation from a classical source, 1 GM = 10^{-50} cm² photon⁻¹ s⁻¹ molecule⁻¹

much smaller classical TPACS than molecules A or C, has an entangled TPACS that is very similar to both A and C. In general, as depicted by theory described above, the electronic levels responsible for the classical two-photon process are well understood. However, this finding suggests a possible different

mechanism for the entangled photon two-photon process in organic materials.

Another striking contrast to this effect was that for molecules E–G, no entangled photon absorption was obtained in our experiments. This result is obtained despite their large classical TPA cross sections. These materials undergo TPA through a direct transition based on the large change in permanent dipole moment between ground and excited states. This mechanism does not require that intermediate states be close to resonance with the photons. Experiments with molecules E–G were carried out in solution at low concentration, very high concentrations, and even in thin films. In each case, no entangled photon absorption could be found in these systems. This result turned out to be very intriguing and completely unexpected. A number of reproducible experiments were performed on these materials to check the validity that in some cases a material could have a large classical nonlinear response, and the same material show no entangled nonlinear response. Later we found the opposite to be true in some cases as well. Depending on the electronic states accessible, an organic material with a relatively small classical two-photon cross section may have a large entangled photon cross section. For example, ZnTPP (molecule B) is a molecule with a smaller classical TPA cross section, yet it exhibits a strong ETPA cross section. These results offer an opportunity for scientists and engineers to tune the quantum entangled nonlinear process, but to do so, one must provide an understanding of the entangled ETPA process.

To interpret why some materials with a large classical TPACS do not appear to absorb entangled photons, we explore the origin of the TPACS. For a non-centrosymmetric molecule, one can consider a three-level system involving ground state *g*, intermediate state *j*, and final state *f*. As previously stated, the TPACS δ_R is given¹⁶ by eq 3. TPA typically occurs via^{20,30} one of two pathways, a virtual state pathway or a permanent dipole pathway, depending on the material, with the TPA rate increasing quadratically with photon flux¹⁶ regardless of the mechanism. However, one cannot directly infer which pathway is utilized from first glance when using eq 1. To directly compare absorption mechanisms for both TPA and ETPA we now modify eqs 1 and 2 to include and distinguish both pathways.

The classical TPACS δ_R can be rewritten¹⁸ as:

$$\delta_R = \frac{B}{\hbar^2 \epsilon_0^2} \omega_0^2 \delta(\epsilon_f - \epsilon_g - 2\omega_0) \left| \frac{1}{(\omega_0 + \epsilon_g - \epsilon_e) - i\kappa_e/2} \mu_{fe} \cdot e \mu_{eg} \cdot e + \frac{1}{\omega_0 - i\kappa_g/2} \mu_{fg} \cdot e \mu_{gg} \cdot e + \frac{1}{-\omega_0 - i\kappa_f/2} \mu_{ff} \cdot e \mu_{fg} \cdot e \right|^2 \quad (4)$$

assuming only photons of the same polarization in classical case. The first term in eq 4 describes TPA through an intermediate level (A), whereas the second and third term describe a process involving permanent dipoles (B). In the classical case these two terms can be simplified to one contribution proportional to permanent dipole difference $\Delta\mu_{fg} = \mu_{ff} - \mu_{gg}$ which gives eq 1.

Two potential pathways for TPA are observed in the two terms of eq 4 and illustrated in Figure 3. The transition dipole

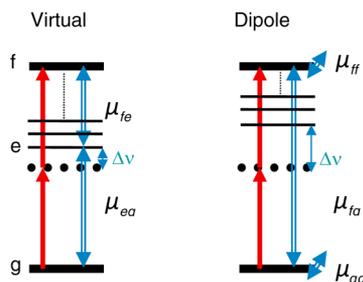


Figure 3. Schematic depiction of two-photon absorption pathways. The intermediate state (left) and dipole (right) pathways of classical two-photon absorption are illustrated and μ is the transition dipole moment. The final, intermediate, and ground states are denoted by f, e, and g, respectively. Photon energies and transition dipole moments are represented by filled and hollow arrows, respectively.

pathway (A), given by the first term, involves an intermediate state (close to resonance with the photon). The transition dipole moments μ_{fe} and μ_{eg} as well as the detuning between the laser frequency and the intermediate state are known to play an important role in this TPA mechanism. Materials with moderate donor–acceptor character and without charge-transfer character are described³¹ as absorbing through pathway (A). For absorption mechanisms involving permanent dipole pathways (B) the intermediate state is off resonance and does not play a role. The ground and excited states are connected directly, and resonance between intermediate states and the laser is not required for TPA. In the case of charge-transfer materials, the contribution to the TPACS from the intermediate state terms is overshadowed by the contribution from the difference of permanent dipole moments of the ground and the excited states. In this case, the second and third terms of eq 4 dominate, and the TPACS is explained^{20,30,32} by pathway (B). This is known to occur when the intermediate states of the material are very far from resonance with the photons.

All materials in which we have observed ETPA were previously described^{11,33,34} as having a classical two-photon excitation through pathway (A), in which an intermediate state is involved in the transition. Theoretical investigations have indicated^{24,27,35–37} an enhancement of the ETPA cross section under conditions of near-resonance between entangled photons and an intermediate state. We have previously shown that a G3 porphyrin dendrimer was capable of strongly absorbing entangled photons, with ETPA cross sections measured nearly on the order of the one-photon absorption cross section at half the wavelength. By varying the entanglement time, T_e , the intermediate state energy was estimated to be $9.85 \times 10^3 \text{ cm}^{-1}$. This intermediate state energy is found to be $\sim 4000 \text{ cm}^{-1}$ below the $^1B_u Q_x$ state within the Q band.³³ This supports the theory advanced by Fei et al.³⁸ and Kojima and Nguyen²⁴ that ETPA involves intermediate states.

Whereas literature has suggested^{18,39} that molecules E–G undergo a two-photon transition by the permanent dipole mechanism, in which the substantial change in permanent dipole moment between ground and excited states allows a direct transition, it is a direct coupling of the intermediate states to the ground and final states. This is in part due to the large detuning energy between the photon and the intermediate state, which reduces its amplitude compared with the dipole pathway. The molecule G was shown¹⁸ to have a $1B_u$ band at $20\,600 \text{ cm}^{-1}$, which is $\sim 8000 \text{ cm}^{-1}$ higher in energy than the

entangled photons used in our experiment. From eq 2, the combination of a large detuning energy between the entangled photon and the $1B_u$ band of molecule G and a weak coupling to the intermediate state is expected to have a negative impact on the ETPA cross section of this material, which leads to no measurable ETPA with our current source of entangled photons.

As previously stated, the ETPA cross section is reported to have dependence on the detuning energy between the entangled photon and the intermediate state as well as on the intermediate state linewidth and the transition matrix elements. To account for this dependence in the ETPA cross section, we rewrite eq 2 in the same manner as eq 4. For a system with ground, intermediate, and excited state wave functions $|g\rangle$, $|e\rangle$, and $|f\rangle$, and under a simplified case of a monochromatic pump between signal and idler beam, we derived for σ_e (analog to Fei et al.³⁸):

$$\sigma_e = \frac{A}{\hbar^2 \epsilon_0^2 A_e T_e} \omega_0^2 \delta(\epsilon_f - \epsilon_g - 2\omega_0) \left| \frac{1 - e^{-i(\omega_0 + \epsilon_g - \epsilon_e)T_e - \kappa_e T_e/2}}{(\omega_0 + \epsilon_g - \epsilon_e) - i\kappa_e/2} \mu_{fe} \cdot e_i \mu_{eg} \cdot e_s + \frac{1 - e^{-i\omega_0 T_e - \kappa_g T_e/2}}{\omega_0 - i\kappa_g/2} \mu_{fg} \cdot e_i \mu_{gg} \cdot e_s + \frac{1 - e^{i\omega_0 T_e - \kappa_f T_e/2}}{-\omega_0 - i\kappa_f/2} \mu_{ff} \cdot e_i \mu_{fg} \cdot e_s \right|^2 \quad (5)$$

where A_e and T_e are entanglement area and entanglement time, respectively, ω_0 is the frequency of the signal and idler photons, e_i and e_s are the polarization of signal and idler, ϵ_g , ϵ_e , and ϵ_f are the frequency of the ground, intermediate, and excited states, respectively, μ_{ij} are the transition dipole matrix elements, and κ_j are the state linewidths. A level scheme as depicted in Figure 4 was assumed; three pathways contribute to this scheme: ETPA

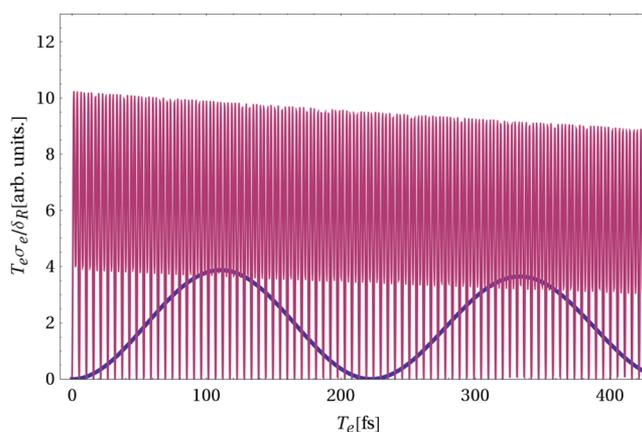


Figure 4. Variation of TPA signal with entanglement time for the two theoretical models depicted in Figure 3 through intermediate levels (blue) and for a model with dominant permanent dipole mechanism (red) where the y axis is T_e (the entanglement time) multiplied by σ_e (the entanglement cross section) divided by the classical/random two-photon absorption cross section (δ_R). The x axis is entanglement time varied over several hundred femtoseconds. $T_e \sigma_e / \delta_R$ is plotted over entanglement time T_e to illustrate the contribution of the material dependent response due to the use of entangled photons.

through an intermediate level $|e\rangle$ and ETPA utilizing permanent dipoles for states $|g\rangle$ and $|f\rangle$. The first term in eq 5 describes ETPA through an intermediate level (A), whereas the second and third terms describe a process involving permanent dipoles (B). In the entangled case we cannot simplify the two terms to one contribution proportional to the permanent dipole difference due to the oscillatory terms in this scenario. Our results suggest that molecules A–D absorb photons via mechanism (A) described by the first term in eq 5, whereas E–G utilize mechanism (B), as described by the second and third terms in eq 5.

We have shown that molecules A–D are capable of strongly absorbing entangled photons, with ETPA cross sections measured nearly on the order of the one-photon absorption cross section using longer excitation wavelengths. It is clear from the data and the cross sections that are reported in Table 1 that there seems to be a nonclassical fluorescence enhancement. This enhancement is perhaps most clearly demonstrated by the fact that we were able to observe a relatively high fluorescent count rate for such a relatively small input flux. To explain the enhancement of ETPEF and the ETPA cross sections over TPEF and the TPA cross sections, we now compare eqs 4 and 5. The material enhancement of ETPA over TPA is visible in the equation with a factor proportional to $(1/T_e A_e)$. However, this factor does not explain the material dependent response to entangled photons. The important terms in eq 5 are the oscillating terms of the form $1 - e^{i\Delta\omega T_e}$ for each of the contributions. We plot $(T_e \sigma_e / \delta_R)$ over entanglement time T_e in Figure 4 for a model system undergoing ETPA via an intermediate level pathway and for a model system with dominant permanent dipole pathway to illustrate this contribution. For case (A) we see an oscillation over entanglement time T_e with a period in the range of several hundred femtoseconds. Periodic destructive interference and thus entanglement-induced transparency is also seen, as previously pointed out by Fei et al.³⁸ The oscillation frequency is thereby dependent on the detuning between intermediate level and the photons. However, if pathway (B) dominates, the picture is similar except the oscillation pattern is a more complex beating pattern controlled by the two permanent dipoles and the period is much shorter. The oscillation period and the distance between the entanglement-induced transparencies is in the range of a few femtoseconds. Therefore, for the permanent dipole case the TPA signal is more likely to be in an area of entanglement-induced transparency. In this case, the oscillation frequency is controlled by and equal to the photon energy. The entanglement time of $T_e \approx 100$ fs used in our experiments may often match values of entanglement-induced transparency inside the inhomogeneous distribution of molecules transition frequencies for all materials dominated by pathway (B) because the values of entangled induced transparency are very dense.

In summary, we have now demonstrated entangled two-photon excited fluorescence on a set of nonlinear organic optical materials. With our method, we utilize the 10 orders of magnitude enhancement previously seen in ETPA experiments to detect measurable emission. This highly efficient nonlinear fluorescence and absorption is expected to have a large impact in quantum imaging, lithography, microscopy, and remote sensing. We have also demonstrated ETPA experiments on a set of nonlinear organic optical materials. Theoretical investigations have predicted^{24,27} that intermediate states far from resonance are not expected to contribute to the entangled

TPACS of a material. Our study has also provided both experimental and theoretical proof that intermediate states may be used to tune the ETPA process. This provides the possibility of observing fluorescence in some materials that actually have very small classical two-photon cross sections. It was also found that the entanglement times used in our experiments may match values of entanglement-induced transparency for all materials dominated by a particular pathway involving intermediate states. These results and theoretical predictions provide a new construct as to how certain materials may now be illuminated by undetectable photons and may be selectively illuminated by classical or nonclassical light.

■ ASSOCIATED CONTENT

Supporting Information

Description of the experimental setup, the instrument correction factors, an explanation of the ETPA cross-section calculation and last, the plotted ETPA rates for samples A–G.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tgoodson@umich.edu.

Present Address

^{||}M. Harpham and O. Suzer: Argonne National Laboratory, Lemont, IL 60439.

Notes

The authors declare no competing financial interest.

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