THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCL

Letter

Hot-Band Absorption Can Mimic Entangled Two-Photon Absorption

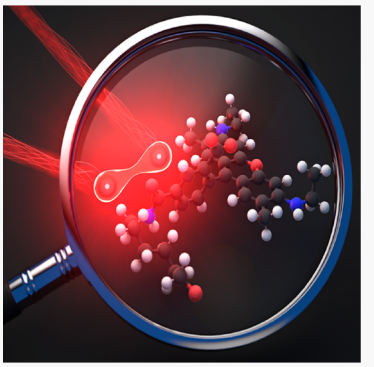
Alexander Mikhaylov, Ryan N. Wilson, Kristen M. Parzuchowski, Michael D. Mazurek, Charles H. Camp, Jr., Martin J. Stevens, and Ralph Jimenez*

Cite This: *J. Phys. Chem. Lett.* 2022, 13, 1489−1493

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

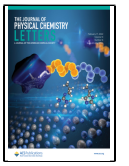
ABSTRACT: It has been proposed that entangled two-photon absorption (E2PA) can be observed with up to 10^{10} lower photon flux than its classical counterpart, therefore enabling ultralow-power two-photon fluorescence microscopy. However, there is a significant controversy regarding the magnitude of this quantum enhancement in excitation efficiency. We investigated the fluorescence signals from Rhodamine 6G and LDS798 excited with a CW laser or an entangled photon pair source at ∼1060 nm. We observed a signal that originates from hot-band absorption (HBA), which is one-photon absorption from thermally populated vibrational levels of the ground electronic state. This mechanism, which has not been previously discussed in the context of E2PA, produces a signal with a linear power dependence, as would be expected for E2PA. For the typical conditions under which E2PA measurements are performed, contributions from the HBA process could lead to a several orders of magnitude overestimate of the quantum advantage.



The implementation of nonclassical light sources in spectroscopic and sensing methods has been a long-standing goal for advancing many practical applications of quantum science. One particularly intriguing possibility is to use a time−energy entangled photon pair source for two-photon absorption (2PA) excitation instead of a coherent, laser-based (classical) source. Here we refer to the latter regime as classical two-photon absorption (C2PA). It has been predicted that if entangled photons generated via spontaneous parametric down conversion (SPDC) are used for excitation, then the resulting entangled two-photon absorption (E2PA) rate should scale linearly with the excitation flux, and the process efficiency can be boosted relative to C2PA at low photon flux.[1,2] Entangled photon excitation might therefore enable ultralow-power two-photon excited fluorescence imaging, which would be particularly advantageous for limiting perturbation and damage of fragile biological samples. The favorable scaling behavior stems from the linear dependence of the 2PA rate on the second-order correlation function, $g^{(2)}$.[3,4] In addition to this absorption efficiency enhancement from the photon statistics, further enhancement is possible from the spectral shape and bandwidth of the frequency anticorrelated photon pairs.[5,6] Whether these mechanisms can provide a practical advantage for E2PA in molecules is still unclear.

Since 2004, numerous publications have reported E2PA and entangled two-photon excited fluorescence (E2PEF) for many different chromophores, reporting large excitation efficiencies.[7−14] The resulting E2PA cross sections, σ_{E2PA}, may be as large as 10^{-17} cm^2, which is on the same order of magnitude as a moderately strong one-photon absorption (1PA) transition. More recently, however, a number of studies have reported conflicting results which cast doubt on the large enhancements claimed in those reports.[15−19] For example, three different groups employed E2PEF measurements to determine the σ_{E2PA} of Rhodamine 6G (Rh6G).[4,20,21] Tabakaev et al.[20] measured E2PEF using CW SPDC excitation at 1064 nm with up to 5×10^8 pairs/s. Although several tests were performed to rule out one-photon mechanisms as the origin of the measured signal, the observed dependence on time delay was inconsistent with expectations.[22] The authors concluded that σ_{E2PA} was 9.9×10^{-22} cm^2 to 1.9×10^{-21} cm^2 for a range of fluorophore concentrations. In a separate study, Parzuchowski et al.[4] observed no E2PEF using a pulsed SPDC excitation source at 810 nm with $\sim 9 \times 10^9$ photons/s. This result was used to determine an upper bound on the cross section for Rh6G of $\sigma_{E2PA} \leq 1.2 \times 10^{-25}$ cm^2, which is nearly 4 orders of magnitude smaller than the value reported by Tabakaev et al.[20] The null result of Parzuchowski et al. was supported by results from a study by Landes et al.[21] In this case, a CW SPDC excitation source at 1064 nm with 2×10^9 pairs/s was used along with dispersion control and sum frequency generation measurements to optimize the excitation radiation parameters and the signal collection efficiency. However, no measurable E2PEF was observed.[21] The origin of the ∼10000-fold variation in reported σ_{E2PA} values is unclear.

Received: November 17, 2021
Accepted: February 1, 2022
Published: February 7, 2022



https://doi.org/10.1021/acs.jpclett.1c03751
J. Phys. Chem. Lett. 2022, 13, 1489−1493

Here we focus on hot-band absorption (HBA) which can contribute to signals measured with SPDC and mimic certain characteristics of E2PA. HBA is a classical 1PA process from the thermally populated vibronic levels of the ground electronic state. Figure 1 shows a schematic of a two electronic level system (solid gray lines) with vibronic levels of the ground state indicated by dashed gray lines. A 2PA transition is allowed between these two electronic states (blue vertical arrows, Figure 1a). If the excitation source has a broad spectrum or is tuned far away from the peak of the "0−0" transition, its radiation can stimulate transitions involving the vibronic manifold of the ground electronic state. If 1PA transitions between these levels and the upper electronic state are allowed, HBA may take place (red vertical arrows, Figure 1b). Although the probability of HBA transitions is very low, C2PA is also inefficient; thus, the magnitude of the signals from the two processes can be comparable under certain conditions. The system relaxes back to the ground electronic state emitting fluorescence photons ("anti-Stokes" emission; green vertical arrows), which are indistinguishable for the two mechanisms.

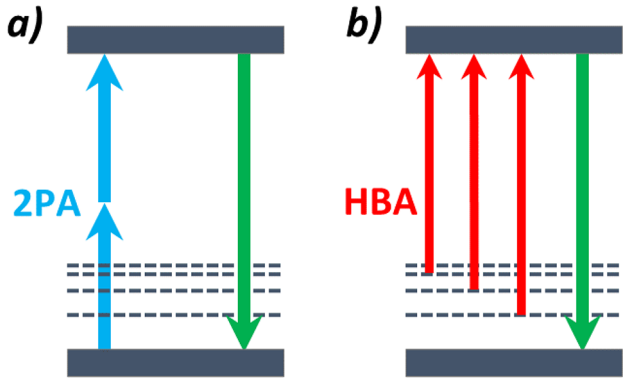


Figure 1. Schematic of 2PA (a) and HBA (b) with electronic and vibronic levels indicated by solid and dashed lines, respectively. The 2PA excitation source (blue) may have high-energy components (red) that resonate with 1PA (hot-band) transitions. Note that the fluorescence emitted by the two mechanisms (green arrows) is indistinguishable.

HBA has been shown to play a crucial role in C2PA measurements[23−28] but has not been discussed in the E2PA literature. The importance of including HBA in the analysis of C2PA data has been detailed in a study by Drobizhev et al.,[25] where C2PA and HBA were simultaneously observed in a series of meso-tetraalkynylporphyrins. In this study, the excitation frequency ν was detuned far to the red of the chromophore's "0−0" transition frequency (ν_{max}) to avoid direct one-photon excitation of the lowest energy transition. However, the detuning ($\nu_{max} - \nu$) was insufficient to avoid excitation from the vibronic manifold of the ground electronic state. Temperature-dependent measurements were conducted to decouple the roles of the two excitation pathways.

An additional complication arises in distinguishing HBA from E2PA by using power dependence. Because HBA is a 1PA process, it scales linearly with excitation power. When the SPDC photon flux is sufficiently low that pairs are separated in time, the E2PA rate is also predicted to scale linearly with excitation power. However, when linear losses act on the produced pairs, E2PA exhibits the unique signature of scaling quadratically with attenuation of the SPDC beam. This behavior is also expected for other two-photon processes, as clearly demonstrated for sum frequency generation.[29] Thus, to confirm the origin of a potential E2PA signal, both power dependencies should be measured. In earlier reports the linear dependence on the pump laser (for SPDC generation) power alone was taken as proof that the signals originated from E2PA. However, this signature is consistent with many one-photon mechanisms,[4] including HBA. This amalgamation of signals, corrupting the purely quantum-enhanced 2PA signal, would lead to misleading conclusions regarding the efficiency of E2PA and its dependence on molecular properties and on the quantum state of the light.

Here we report 2PA measurements on Rh6G and LDS798 (CAS No. 92479-59-9) dissolved in methanol and deuterated chloroform ($CDCl_3$), respectively. Rh6G is particularly interesting because it was studied in the prior E2PA reports mentioned above and has well-known C2PA properties.[30] LDS798 is another commercially available fluorophore with a large C2PA cross section at 1064 nm.[31,32] According to a simple probabilistic model of the E2PA process proposed in Fei et al.,[33] a large C2PA cross section implies a large E2PA

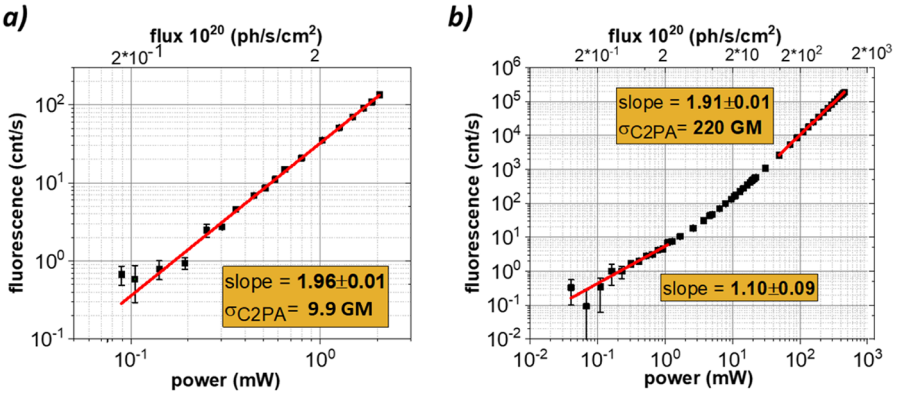


Figure 2. Results of classical (coherent) two-photon excited fluorescence measurements on a log−log scale. Fluorescence signals (vertical axis, in counts per second, cnt/s) versus the laser excitation power (lower horizontal axis, in mW) or versus the excitation photon flux (upper horizontal axis, in photons per second per cm^2, ph/s/cm^2) measured for Rh6G and LDS798 are shown in panels a and b, respectively (black squares). The slope values obtained from the fit (red lines) and the derived cross-section values in GM units are indicated in the insets. In the case of LDS798 the slope value changes from quadratic (1.91) to nearly linear (1.10) with decreasing power. Error bars correspond to one standard deviation.

https://doi.org/10.1021/acs.jpclett.1c03751
J. Phys. Chem. Lett. 2022, 13, 1489−1493

cross section as well. We use two CW sources operated near 1060 nm —a laser and time-energy entangled photon pairs generated via SPDC—to independently excite the samples under identical conditions. We observe no measurable E2PEF signal from Rh6G with the maximum available SPDC power. In contrast, a signal is observed from the LDS798 sample. Upon further investigation, we find this signal does not show the excitation power scaling characteristics of E2PA. We attribute this fluorescence signal to HBA. Temperature-dependent measurements, excitation wavelength-dependent measurements, and modeling of the signals support our conclusions. We propose that HBA may be responsible for absorption signals observed with SPDC excitation. We emphasize the importance of including additional verification tests to elucidate the origin of signals measured with SPDC excitation.

A detailed description of the experimental setup and the measurement procedures is provided in the Supporting Information. Classical two-photon excited fluorescence (C2PEF) measurements on Rh6G were used to ensure the proper alignment of the optical system and characterize its sensitivity. In Figure 2, the detected fluorescence signal for classical excitation is plotted versus the excitation photon flux or the excitation power on a log−log scale. The minimum count rate that we could assign to fluorescence photons measured above the background level (3 cnt/s to 5 cnt/s) is determined to be ∼0.5 cnt/s. The power dependence of C2PEF for Rh6G (Figure 2a) in the range 0.1 mW to 2 mW is found to be near-quadratic with a slope (power exponent) of 1.96 ± 0.01. The sample concentration (1.1×10^{-3} mol/L), fluorescence quantum yield (0.9[34]), and the measured and calculated excitation condition parameters are used to derive the value of the C2PA cross section, σ_{C2PA} = 9.9 GM (see details in the Supporting Information), which agrees with the literature value of 9.8 GM.[30]

We repeat the C2PEF measurement with LDS798, which has a large σ_{C2PA}, but is less advantageous for fluorescence detection because its quantum yield is only 0.054 (see the Supporting Information), and its emission spectrum is red-shifted from the peak of the detector sensitivity (Figure S3). Makarov et al.[31] reported σ_{C2PA} of 515 GM for LDS798 excited at 1060 nm. This value was probably overestimated by a factor of 2 due to an issue with a Rhodamine B reference standard used in that work as was discussed in de Reguardati et al.[30] In our experiment the C2PEF power dependence in the range 50 mW to 500 mW is found to have a slope value of 1.91 ± 0.01 (Figure 2b). Using a sample of 10^{-4} mol/L LDS798, we derive σ_{C2PA} = 220 GM.

The methods and apparatus used here are very similar to ones employed in our earlier study,[4] where the uncertainty for determining σ_{C2PA} was estimated to be ∼28%. We therefore assume it is similar in the present experiment.

Upon decreasing the excitation power for LDS798, we observe that the slope of the power dependence decreases and reaches a value of 1.10 ± 0.09 in the 5×10^{-5} W to 10^{-3} W range. Overall, the data show a transition from a quadratic (i.e., C2PA) to a linear (i.e., 1PA) excitation regime. Although a transition of this type is rather uncommon in C2PEF experiments, there are several reports of similar behavior indicating the presence of the HBA process.[23−28] As suggested by Drobizhev et al.,[25] the collected fluorescence signal, F (in cnt/s), can be written as a sum of two terms, one describing the excitation via HBA and the other via C2PA

$$F = NK\sigma_{HBA}\phi + \frac{1}{2}NK\sigma_{C2PA}\phi^2 \quad (1)$$

where N is the number of molecules in the excitation volume, K is the overall fluorescence collection efficiency, ϕ is the excitation photon flux, and σ_{HBA} is the HBA cross section. The σ_{HBA} is a function of the excitation frequency ν and sample temperature T (see the Supporting Information for details). Lowering the temperature is expected to decrease the rate of HBA but not affect the rate of C2PA. In our temperature-dependent experiments (see the Supporting Information), we observe a maximum 12 nm red-shift in the steady-state emission spectrum of the fluorophore and 23% decrease in quantum yield while increasing the temperature, both of which are accounted for in the analysis.

Equation 1 indicates that the relative contributions of C2PA and HBA vary with excitation flux. The HBA term depends linearly on excitation power while the C2PA term depends quadratically; thus, at higher powers the latter should be dominant. This is consistent with what we observe in our experiment with LDS798 (see more on this below and in the Supporting Information).

Next, we block the 1060 nm laser and switch to SPDC excitation. For Rh6G we are unable to detect any fluorescence signal with the maximum available SPDC power of ∼1.3 μW. However, for LDS798 we measure a strong fluorescence signal (up to 40 cnt/s) under SPDC excitation (Figure 3). First, we

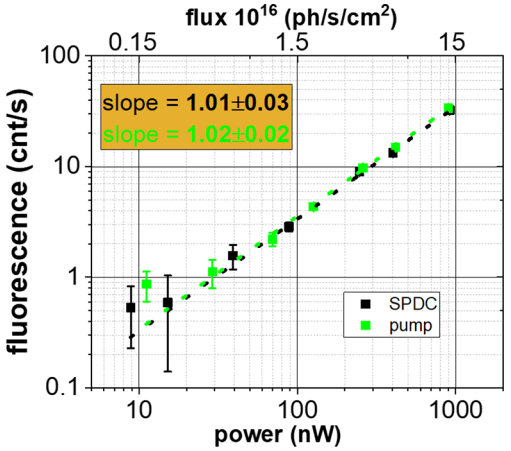


Figure 3. Results of measurements with SPDC excitation of LDS798 on a log−log scale. Fluorescence count rate (in cnt/s) versus the SPDC power (lower horizontal axis, in nW) or the excitation photon flux (upper horizontal axis, in ph/s/cm^2). The SPDC excitation flux is calculated assuming the effective wavelength of 1064 nm. The excitation power was controlled by attenuating the SPDC (black squares) or pump laser (green squares) beams. In both cases the signal dependence was linear as determined by the slope values (shown in the inset) calculated from the fits (dashed black and green line, respectively). Error bars correspond to one standard deviation.

carefully verify that this signal is not a scattered portion of the SPDC light and not related to the solvent itself. Replacing the LDS798 sample with pure $CDCl_3$ results in no signal observed above the background level. To assess whether the signal from the LDS798 sample is E2PEF, we test for a unique signature of the process as discussed above. In two separate measurements, we vary the SPDC pump power and attenuate the SPDC beam. Figure 3 is a plot of the measured fluorescence signals versus the excitation power or, equivalently, versus the flux on a log−

https://doi.org/10.1021/acs.jpclett.1c03751
J. Phys. Chem. Lett. 2022, 13, 1489−1493

log scale. Varying the SPDC pump power (green squares), we observe that the fluorescence follows a linear dependence (slope value of 1.02 ± 0.02), which is consistent with E2PEF. However, attenuation of the SPDC beam power (black symbols) also results in a linear dependence (slope value of 1.01 ± 0.03). The latter result clearly indicates that the fluorescence signal is not related to E2PA because attenuating the SPDC beam with a neutral density filter randomly removes individual photons rather than photon pairs, thus making the excitation more classical, and classical 2PA scales quadratically with power.

We perform two additional experiments that confirm the observation of HBA. We characterized the temperature dependence of the C2PA signal from LDS798 encapsulated in a polydimethylsiloxane (PDMS) matrix. A rigid polymer rather than a liquid is selected to ensure that changes in solvent viscosity with temperature do not influence the radiationless relaxation rate of LDS798 and thus its fluorescence quantum yield.[35] The fluorescence signal in PDMS was observed to increase nearly 4-fold with increasing temperature from 283 K to 323 K and is well fit by a Boltzmann function (Figure S4a). The experiment was repeated with SPDC excitation (Figure S4b,c). The measured signal scales with temperature in the same manner. In addition, we used an independent setup designed for characterizing absorption cross sections[32] to measure the HBA cross section of LDS798 as a function of wavelength in the 680 nm to 900 nm region. We compared this to the cross section we derived from the data shown in Figure 2b. The cross sections in the red tail region, including our 1060 nm data point, fit to a Boltzmann function (Figure S8), which is consistent with HBA theory (eq 6 in the SI). Finally, we note that a model entirely based on HBA without any adjustable parameters is consistent with both the laser-excited and SPDC-excited fluorescence signals (Figure S7).

Several important points can be concluded from this study. We have shown that even when the excitation wavelengths are detuned hundreds of nanometers from the 1PA peaks of a chromophore, vibronic states can still be excited via HBA. Although this effect is known from previous reports on C2PA, it has not been discussed in previous studies of E2PA. Explaining the origin of inconsistency among different experiments is the most significant challenge currently facing the development of E2PA spectroscopy and its applications. As shown here for LDS798, the HBA signal can partially mimic the power scaling of E2PA. It seems likely that this mechanism could be contributing to E2PA measurements on any other chromophore. Potential HBA contributions should be carefully quantified since they could lead to a significant overestimate of the quantum enhancement for the 2PA efficiency. Our results underline a critical need to perform stringent tests for unique signatures of E2PA in measured signals with SPDC excitation to distinguish one-photon processes from E2PA. In particular, to confirm a signal is from E2PA as opposed to other potential mechanisms, the proper validation procedure is to vary the incident power from the entangled photon source both by attenuating the power input to the SPDC crystal and also by attenuating the power afterward. To demonstrate E2PEF, these two methods of varying the incident power must show different fluorescence power dependencies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c03751.

Details of the experimental setup, applied measurement procedures, σ_{C2PA} calculations, temperature-dependent measurements, modeling the measured HBA signal, and measurements of HBA cross section as a function of wavelength (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Ralph Jimenez − *JILA, 440 UCB, University of Colorado, Boulder, Colorado 80309, United States; Department of Chemistry, 215 UCB, University of Colorado, Boulder, Colorado 80309, United States;* orcid.org/0000-0002-8989-405X; Email: rjimenez@jila.colorado.edu

Authors

Alexander Mikhaylov − *JILA, 440 UCB, University of Colorado, Boulder, Colorado 80309, United States;* Present Address: Max Planck Institute for the Science of Light, Staudtstrasse 2, 91058 Erlangen, Germany

Ryan N. Wilson − *JILA, 440 UCB, University of Colorado, Boulder, Colorado 80309, United States; Department of Physics, 390 UCB, University of Colorado, Boulder, Colorado 80309, United States*

Kristen M. Parzuchowski − *JILA, 440 UCB, University of Colorado, Boulder, Colorado 80309, United States; Department of Physics, 390 UCB, University of Colorado, Boulder, Colorado 80309, United States*

Michael D. Mazurek − *National Institute of Standards and Technology, Boulder, Colorado 80305, United States; Department of Physics, 390 UCB, University of Colorado, Boulder, Colorado 80309, United States*

Charles H. Camp, Jr. − *National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States*

Martin J. Stevens − *National Institute of Standards and Technology, Boulder, Colorado 80305, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.1c03751

Author Contributions

A.M., R.N.W., and K.M.P. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge Mikhail Drobizhev (Montana State University) for suggesting that we closely examine the HBA contributions and for the technical help with some of the measurements. Some of the experimental results were obtained by using his resource for multiphoton characterization of genetically encoded probes, supported by the NIH/NINDS Grant U24NS109107. A.M. and K.M.P. thank Srijit Mukherjee for assisting with the 1PA measurements and for valuable discussions in preparation of the manuscript. We thank Steven Burrows for preparing the table of contents graphic. This work was supported by NIST and by the NSF Physics Frontier Center at JILA (PHY 1734006) and by the NSF-STROBE Center (DMR 1548924). Certain commercial equipment, instruments, or materials are identified in this paper in order to

specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

REFERENCES

(1) Gea-Banacloche, J. Two-Photon Absorption of Nonclassical Light. *Phys. Rev. Lett.* **1989**, *62*, 1603−1606.
(2) Javanainen, J.; Gould, P. L. Linear Intensity Dependence of a Two-Photon Absorption Rate. *Phys. Rev. A* **1990**, *41*, 5088−5091.
(3) Mollow, B. Two-Photon Absorption and Field Correlation Functions. *Phys. Rev.* **1968**, *175*, 1555−1563.
(4) Parzuchowski, K. M.; Mikhaylov, A.; Mazurek, M. D.; Wilson, R. N.; Lum, D. J.; Gerrits, T.; Camp, C. H., Jr.; Stevens, M. J.; Jimenez, R. Setting Bounds on Entangled Two-Photon Absorption Cross Sections in Common Fluorophores. *Phys. Rev. Appl.* **2021**, *15*, 044012.
(5) Raymer, M. G.; Landes, T.; Allgaier, M.; Merkouche, S.; Smith, B. J.; Marcus, A. H. Two-Photon Absorption of Time-Frequency-Entangled Photon Pairs by Molecules: The Roles of Photon-Number Correlations and Spectral Correlations. *arXiv:2012.05375* [quant-ph] **2020**.
(6) Carnio, E. G.; Buchleitner, A.; Schlawin, F. How To Optimize the Absorption of Two Entangled Photons. *SciPost Phys. Core* **2021**, *4*, 028.
(7) French, R. E.; Goodson, T. G. Applications Of Correlated Photon Statistics With a Biphoton Source in an Organic Material. *Proc. SPIE* **2004**, 5161.
(8) Lee, D.-I.; Goodson, T. Entangled Photon Absorption in an Organic Porphyrin Dendrimer. *J. Phys. Chem. B* **2006**, *110*, 25582−25585.
(9) Harpham, M. R.; Suzer, O.; Ma, C.-Q.; Bauerle, P.; Goodson, T. Thiophene Dendrimers as Entangled Photon Sensor Materials. *J. Am. Chem. Soc.* **2009**, *131*, 973−979.
(10) Guzman, A. R.; Harpham, M. R.; Suzer, O.; Haley, M. M.; Goodson, T. G. Spatial Control of Entangled Two-Photon Absorption with Organic Chromophores. *J. Am. Chem. Soc.* **2010**, *132*, 7840−7841.
(11) Upton, L.; Harpham, M.; Suzer, O.; Richter, M.; Mukamel, S.; Goodson, T. Optically Excited Entangled States in Organic Molecules Illuminate the Dark. *J. Phys. Chem. Lett.* **2013**, *4*, 2046−2052.
(12) Varnavski, O.; Pinsky, B.; Goodson, T. Entangled Photon Excited Fluorescence in Organic Materials: An Ultrafast Coincidence Detector. *J. Phys. Chem. Lett.* **2017**, *8*, 388−393.
(13) Villabona-Monsalve, J. P.; Varnavski, O.; Palfey, B. A.; Goodson, T. Two-Photon Excitation of Flavins and Flavoproteins with Classical and Quantum Light. *J. Am. Chem. Soc.* **2018**, *140*, 14562−14566.
(14) Kang, G.; Avanaki, K. N.; Mosquera, M. A.; Burdick, R. K.; Villabona-Monsalve, J. P.; Goodson, T.; Schatz, G. C. Efficient Modeling of Organic Chromophores for Entangled Two-Photon Absorption. *J. Am. Chem. Soc.* **2020**, *142*, 10446−10458.
(15) Ashkenazy, A.; Wang, K.; Unternährer, M.; Fixler, D.; Stefanov, A. Estimation Of the Rate of Entangled-Photon Pair Interaction With Metallic Nanoparticles Based on Classical-Light Second-Harmonic Generation Measurements. *J. Phys. B: At. Mol. Opt. Phys.* **2019**, *52*, 145401−145411.
(16) Mikhaylov, A.; Parzuchowski, K. M.; Mazurek, M. D.; Lum, D. J.; Gerrits, T.; Champ, C. H.; Stevens, M. J.; Jimenez, R. A Comprehensive Experimental System for Measuring Molecular Two-Photon Absorption Using an Ultrafast Entangled Photon Pair Excitation Source. *Proc. SPIE* **2020**, 11295.
(17) Corona-Aquino, S.; Calderón-Losada, O.; Li-Gómez, M. Y.; Cruz-Ramirez, H.; Alvarez-Venicio, V.; del Pilar Carreón-Castro, M.; de J. León-Montiel, R.; U'Ren, A. B. Experimental Study on the Effects of Photon-Pair Temporal Correlations in Entangled Two-Photon Absorption. *arXiv:2101.10987* **2021**.
(18) Raymer, M. G.; Landes, T.; Allgaier, M.; Merkouche, S.; Smith, B. J.; Marcus, A. H. How Large Is the Quantum Enhancement of Two-Photon Absorption by Time-Frequency Entanglement of Photon Pairs? *Optica* **2021**, *8*, 757−758.
(19) Landes, T.; Raymer, M. G.; Allgaier, M.; Merkouche, S.; Smith, B. J.; Marcus, A. H. Quantifying the Enhancement of Two-Photon Absorption Due to Spectral-Temporal Entanglement. *Opt. Exp.* **2021**, *29*, 20022−20033.
(20) Tabakaev, D.; Montagnese, M.; Haack, G.; Bonacina, L.; Wolf, J.-P.; Zbinden, H.; Thew, R. T. Energy-Time-Entangled Two-Photon Molecular Absorption. *Phys. Rev. A* **2021**, *103*, 033701.
(21) Landes, T.; Allgaier, M.; Merkouche, S.; Smith, B. J.; Marcus, A. H.; Raymer, M. G. Experimental feasibility of molecular two-photon absorption with isolated time-frequency-entangled photon pairs. *Phys. Rev. Research* **2021**, *3*, 033154.
(22) Lavoie, J.; Landes, T.; Tamimi, A.; Smith, B. J.; Marcus, A. H.; Raymer, M. G. Phase-Modulated Interferometry, Spectroscopy, and Refractometry using Entangled Photon Pairs. *Adv. Quan. Techn.* **2020**, *3*, 1900114.
(23) Apatin, V.; Makarov, G. Multiphoton Absorption of Infrared Laser Radiation by SF_6 Molecules Cooled in a Supersonic Jet. *Zh. Eksp. Teor. Fiz.* **1983**, *84*, 15−29.
(24) Okamura, H.; Tosa, V.; Ishii, T.; Takeuchi, K. Collisional Effects in the IR Multiphoton Absorption and Dissociation Of Si_2F_6. *J. of Photochem. and Photobiol. A:Chem.* **1996**, *95*, 203−207.
(25) Drobizhev, M.; Karotki, A.; Kruk, M.; Krivokapic, A.; Anderson, H. L.; Rebane, A. Photon Energy Upconversion in Porphyrins: One-Photon Hot-Band Absorption Versus Two-Photon Absorption. *Chem. Phys. Lett.* **2003**, *370*, 690−699.
(26) Makarov, N.; Drobizhev, M.; Rebane, A.; Peone, D.; Wolleb, H.; Spahni, H.; Makarova, E.; Lukyanets, E. Resonance Enhancement of Two-Photon Absorption of Phthalocyanines for 3D Optical Storage in the Presence of Hot-Band Absorption. *Proc. SPIE* **2007**, 6470.
(27) Rebane, A.; Makarov, N.; Drobizhev, M.; Spangler, C. W.; Gong, A.; Meng, F. Broad Bandwidth Near-IR Two-Photon Absorption in Conjugated Porphyrin-Core Dendrimers. *Proc. SPIE* **2007**, 6653.
(28) Starkey, J. R.; Rebane, A. K.; Drobizhev, M. A.; Meng, F.; Gong, A.; Elliott, A.; McInnerney, K.; Spangler, C. W. New Two-Photon Activated Photodynamic Therapy Sensitizers Induce Xenograft Tumor Regressions After Near-IR Laser Treatment Through the Body of the Host Mouse. *Clin. Cancer Res.* **2008**, *14*, 6564−6573.
(29) Dayan, B.; Pe'er, A.; Friesem, A. A.; Silberberg, Y. Nonlinear Interactions With an Ultrahigh Flux of Broadband Entangled Photons. *Phys. Rev. Lett.* **2005**, *94*, 043602.
(30) de Reguardati, S.; Pahapill, J.; Mikhailov, A.; Stepanenko, Y.; Rebane, A. High-Accuracy Reference Standards for Two-Photon Absorption in the 680−1050 nm Wavelength Range. *Opt. Exp.* **2016**, *24*, 9053−9066.
(31) Makarov, N. S.; Campo, J.; Hales, J. M.; Perry, J. W. Rapid, Broadband Two-Photon-Excited Fluorescence Spectroscopy and its Application to Red-Emitting Secondary Reference Compounds. *Opt. Mater. Exp.* **2011**, *1*, 551−563.
(32) Drobizhev, M.; Molina, R. S.; Hughes, T. E. Characterizing the Two-Photon Absorption Properties of Fluorescent Molecules in the 680−1300 nm Spectral Range. *Bio Protoc* **2020**, *10*, 1−47.
(33) Fei, H.-B.; Jost, B. M.; Popescu, S.; Saleh, B. E. A.; Teich, M. Entangled-Induced Two-Photon Transparency. *Phys. Rev. Lett.* **1997**, *78*, 1679−1682.
(34) Penzkofer, A.; Leupacher, W. Fluorescence Behaviour of Highly Concentrated Rhodamine 6G Solutions. *J. of Lum.* **1987**, *37*, 61−72.
(35) Doan, H.; Castillo, M.; Bejjani, M.; Nurekeyev, Z.; Dzyuba, S. V.; Gryczynski, I.; Gryczynski, Z.; Raut, S. Solvatochromic Dye LDS 798 As Microviscosity and pH Probe. *Phys. Chem. Chem. Phys.* **2017**, *19*, 29934−29939.

https://doi.org/10.1021/acs.jpclett.1c03751
J. Phys. Chem. Lett. 2022, 13, 1489−1493