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Spatial Control of Entangled Two-Photon Absorption with Organic Chromophores

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Organic conjugated nonlinear optical (NLO) macromolecules have been used in a variety of important optical applications.[1] One relatively unexplored area for organic NLO materials is the absorption and detection of entangled photons generated by spontaneous parametric down-conversion (SPDC). Entangled two-photon absorption (ETPA) in real materials may be very useful for applications in quantum sensing and communication as well as new methods of spectroscopy at extremely low input photon fluxes.[2,3] ETPA has been successfully performed for a variety of organic two-photon absorbing materials with a very small number of photons.[4,5] However, there have been no reports of the control of the ETPA process through different quantum-entangled states of the photons. The SPDC in β-BaB_2O_4 (BBO) crystals results in signal and idler daughter photons governed by the so-called phase-matching conditions $\omega_p = \omega_s + \omega_i$ and $\mathbf{k}_p = \mathbf{k}_s + \mathbf{k}_i$, where the subscripts p, s, and i denote pump, signal, and idler photons, respectively.[6,7] Phase matching also dictates the spatiotemporal characteristics of the SPDC emission.[7] Three distinct spatial orientations of the resulting emission pattern have been found, and in this manuscript it is shown that these patterns also allow a method of either enhancing or limiting the degree of entangled photon absorption in an organic material. The particular mechanism and cause for varying amounts of ETPA is also discussed in reference to controlling the entangled photon absorption process.

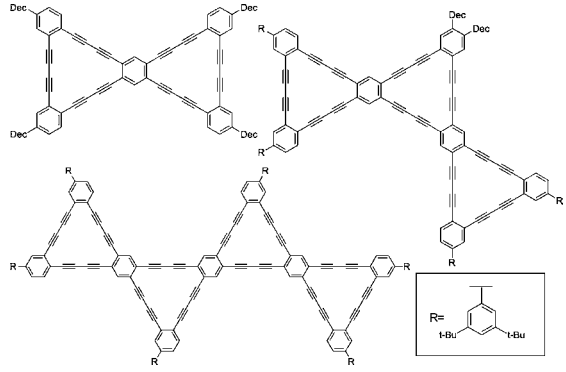

Figure 1. Annulene systems: (top left) bis[18]annulene; (top right) tri[18]annulene; (bottom) "linear" tetra[18]annulene.

Figure 1 shows the structures of the two-photon-absorbing macromolecules used in this investigation.[8] The bisannulene system and similar structures have shown very impressive two-photon absorption (TPA) cross sections with classical photons.[9,10] Our investigation showed an unprecedented enhancement due to delocalized excitons for the tri- and tetraannulene systems (see Table 1). The measurement of classical TPA cross sections followed that of refs 9 and 10 and is detailed in the Supporting Information.

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Table 1. Two-Photon and Entangled Two-Photon Cross Sections of Annulene Systems[a]

sample	TPA δ (GM)[b]	phase-matching condition	ETPA σ (10^{-17} cm^2)
bisannulene	150	noncollinear	3.2
		collinear	3.0
		separated	0
triannulene	1650	noncollinear	8.1
		collinear	2.4
		separated	0
tetraannulene	2960	noncollinear	9.9
		collinear	6.7
		separated	0

[a] Cross sections were calculated at an excitation wavelength of 800 nm. [b] 1 GM = 1×10^{-50} cm^4 s photon^{-1}.

ETPA is a process involving entangled photon pairs that populate excited (or virtual) states of a molecule with a finite interaction time (the entanglement time) and area (the entanglement area). Shown in Table 1 are the ETPA cross sections for the annulene materials, which are tabulated for different phase-matching conditions. A description of the experimental setup for ETPA can be found in the Supporting Information.[4,5] These cross sections were calculated utilizing a simplified theory for ETPA.[11] The total absorption rate is expressed as[11]

$$R = \sigma_e \phi + \delta_r \varphi^2 \qquad (1)$$

where σ_e denotes the ETPA cross section, which gives a linear dependence on the input photon flux φ, and δ_r denotes the classical (or random) TPA cross section, which gives a quadratic dependence on φ.

We have found a way to control the ETPA process through the use of the phase-matching conditions from SPDC. Shown in Figure 2 are three images obtained from the different controlled phase-matching conditions. The resulting signal and idler fluxes propagate as a pair of polychromatic cones, from which frequency selection yields a pair of rings in the transverse plane whose angular distribution depends on the angle of the crystal optical axis relative to the pump beam. The three distinct spatial orientations of the rings are (1) noncollinear, in which the rings overlap in two areas; (2) collinear, in which the rings are tangential, or overlap in one area; and (3) spatially separated, in which there is no spatial overlap. In type-II SPDC, the signal and idler fluxes also carry orthogonal polarizations, making it useful for observation of polarization entanglement.[12]

We carried out ETPA experiments with all three phase-matching conditions for these novel, highly nonlinear two-photon materials. The ETPA collection data are shown in Figure 3, grouped by phase-matching conditions. From the ETPA cross sections in Table 1, a downward trend is observed in going from noncollinear to collinear to spatially separated phase-matching conditions. In addition, the ETPA

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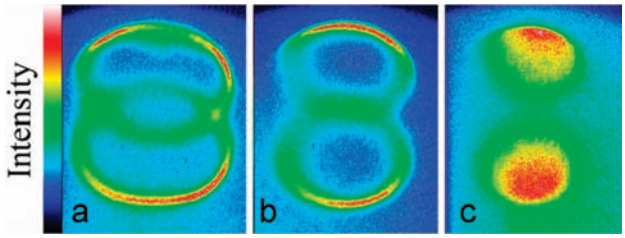

Figure 2. SPDC spatial profiles for (a) noncollinear, (b) collinear, and (c) spatially separated phase-matching conditions.

data for the spatially separated condition show no significant absorption for any of the samples.

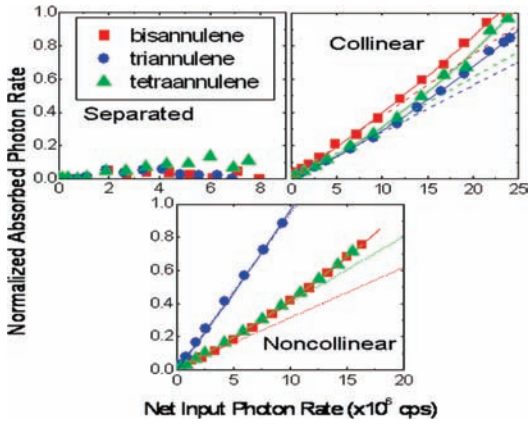

Figure 3. Results of ETPA measurements grouped by phase-matching condition: (top left) spatially separated; (top right) collinear; (bottom) noncollinear. The normalized absorption rates are plotted against the input photon rate. The dashed lines show linear fits, and the solid curves show quadratic fits.

The dependence of the ETPA cross section on the entanglement area A_e and entanglement time T_e were investigated as a possible cause of the variation in absorption characteristics among the phase-matching conditions. The temporal and spatial widths of the fourth-order coherence function, which are given by T_e and A_e, respectively, affect the ETPA cross section σ_e according to the expression[2]

$$\sigma_e(T_e, \tau) = \frac{\pi\omega_p^{\,2}}{16A_eT_e}\delta(\varepsilon_f - \varepsilon_i - \omega_p)s(T_e, \tau) \qquad (2)$$

under degenerate pumping, where

$$s(T_e, \tau) = \left|\sum_j \frac{D_j}{\Delta_j}\{2 - e^{-i\Delta_j(T_e-\tau)} - e^{-i\Delta_j(T_e+\tau)}\}\right|^2 \qquad (3)$$

for signal−idler path delay τ, pump frequency ω_p, energy mismatches Δ_j, and transition matrix elements D_j. A_e has been shown to depend on the beam waist and is not expected to vary with phase-matching condition.[13] The difference in entanglement time among the different phase-matching conditions was 8×10^{-2} fs (see the Supporting Information for the calculation). This small change in T_e could not account for the difference in the ETPA characteristics between the spatially separated case and the other two conditions.

Visibility also offered no explanation for the absence of entangled photon absorption. There was no indication that the visibility for the spatially separated condition should be drastically lower than that for either the collinear or noncollinear condition. The spatially separated case (which showed no ETPA) has previously been shown to exhibit high visibility for SPDC.[14] Our polarization visibility measurements yielded a maximum visibility of 85%, which did not vary significantly among the phase-matching conditions.

In attempts to determine the cause of the dissimilarity in absorption characteristics for the spatially separated condition, it was found that the polarization visibilities, entanglement time, and entanglement area did not vary significantly with the SPDC phase-matching condition. Instead, we suggest that "distinguishability" between the signal and idler fluxes is a significant difference that may have given rise to the changes in ETPA behavior with different phase-matching conditions. The entangled photons are said to be spatially indistinguishable in the regions of overlap of the signal and idler emission cones, where it is impossible to distinguish which photon is the idler and which is the signal in the pair.[15] The noncollinear condition contains two regions of overlap and the collinear condition one region, whereas the spatially separated condition produces no spatial indistinguishability.

These ETPA experiments demonstrate a way to control the amount of absorption of entangled photons by changing the spatial orientation of the SPDC emission pattern. We have shown that the ETPA cross section of conjugated organic molecules decreases as the overlap of the signal and idler photons decreases, with an absence of absorption in the case where there is no overlap. Such a tunable absorption may possibly be utilized in applications such as quantum imaging, sensing, and communication.

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Supporting Information Available: Details of sample preparation, experimental setup, and techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Goodson, T., III. *Acc. Chem. Res.* **2005**, *38*, 99. (b) Goodson, T., III. *Annu. Rev. Phys. Chem.* **2005**, *56*, 581.
(2) Saleh, B. E. A.; Jost, B. M.; Fei, H.-B.; Teich, M. C. *Phys. Rev. Lett.* **1998**, *80*, 3483.
(3) Kojima, J.; Nguyen, Q.-V. *Chem. Phys. Lett.* **2004**, *396*, 323.
(4) Lee, D. I.; Goodson, T., III. *J. Phys. Chem. B* **2006**, *110*, 25582.
(5) Harpham, M. R.; Süzer, Ö.; Ma, C.-Q.; Bäuerle, P.; Goodson, T., III. *J. Am. Chem. Soc.* **2009**, *131*, 973.
(6) Saleh, B. E. A.; Abouraddy, A. F.; Sergienko, A. V.; Teich, M. C. *Phys. Rev. A* **2000**, *62*, 043816.
(7) Kiess, T. E.; Shih, Y. H.; Sergienko, A. V.; Alley, C. O. *Phys. Rev. Lett.* **1993**, *71*, 3893.
(8) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213.
(9) Bhaskar, A.; Ramakrishna, G.; Haley, M. M.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 13972.
(10) Anand, S.; Varnavski, O.; Marsden, J. A.; Haley, M. M.; Schlegel, H. B.; Goodson, T., III. *J. Phys. Chem. A* **2006**, *110*, 1305.
(11) Fei, H.-B.; Jost, B. M.; Popescu, S.; Saleh, B. E. A.; Teich, M. C. *Phys. Rev. Lett.* **1997**, *78*, 1679.
(12) (a) Kwiat, P. G.; Mattle, K.; Weinfurter, H.; Zeilinger, A.; Sergienko, A. V.; Shih, Y. H. *Phys. Rev. Lett.* **1995**, *75*, 4337. (b) Ou, Z. Y.; Mandel, L. *Phys. Rev. Lett.* **1988**, *61*, 50. (c) Hong, C. K.; Mandel, L. *Phys. Rev. A* **1985**, *31*, 2409.
(13) Joobeur, A.; Saleh, B. E. A.; Larchuk, T. S.; Teich, M. C. *Phys. Rev. A* **1996**, *53*, 4360.
(14) Niu, X. L.; Huang, Y. F.; Xiang, G. Y.; Guo, G. C.; Ou, Z. Y. *Opt. Lett.* **2008**, *33*, 968.
(15) Bennink, R. S.; Liu, Y.; Earl, D.; Grice, W. P. *Phys. Rev. A* **2006**, *74*, 023802.

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