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Efficient Three-Photon Excited Deep Blue Photoluminescence and Lasing of Diphenylamino and 1,2,4-Triazole Endcapped Oligofluorenes

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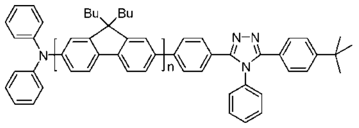
Multiphoton absorption, in particular two-photon and three-photon absorption, has drawn considerable interest over the years because of its potential applications in various optoelectronics and photonics as well as the fundamental physics of nonlinear optics (NLO). Owing to the use of the longer wavelength excitation source and the characteristics of the intensity-dependence of the multiphoton absorption process, the multiphoton absorption offers many advantages for the technological applications of high capacity data storage,[1−3] three-dimensional microfabrication,[4−7] biological imaging,[8] photodynamic therapy,[9,10] and frequency up-converted lasing.[11−13] Despite significant progress in developing organic molecules with large two-photon absorption (TPA) properties over the past decade, the study for structure−three-photon absorption property correlation of organic molecules is rather limited. In principle, donor−acceptor chromophores possessing a highly polarizable π-conjugated system are highly two-photon absorption active; however, it is not guaranteed that they will exhibit an interesting and useful three-photon absorption property such as frequency up-converted lasing. To exhibit multiphoton absorption up-converted lasing, molecules are required to possess high fluorescent quantum efficiency, significant multiphoton absorption cross-section, and low fluorescent reabsorption, which could affect the lasing threshold and the attainment of optical gain. As a result, there are only limited multiphotons particularly three-photon excited fluorescent dyes that can exhibit frequency up-converted lasing.[13] Although there are demonstrations of one-photon excited lasing[14,15] and two-photon pumped lasing from a two-dimensional photonic bandgap structure with ladder-type poly(*p*-phenylene)[16] in the blue light range, to the best of our knowledge, three-photon induced up-converted pure blue-lasing in organic materials has not been demonstrated yet.

We demonstrate herein for the first time the multiphoton absorption and frequency up-converted blue-lasing using a novel homologous series of diphenylamino and 1,2,4-triazole endcapped π-conjugated oligofluorenes, *p*-PhN-OF(*n*)-TAZ where $n = 2-4$ (Figure 1). In addition to the two-photon excited photoluminescence and lasing pumped by 800 nm femtosecond laser pulses, these newly synthesized oligofluorenes exhibit very efficient three-photon excited photoluminescence and lasing pumped at 1.3 μm. The best full width half-maximum (fwhm) of the three-photon lasing is narrower than 6 nm which is the narrowest ever reported. We also demonstrate that the NLO properties of these oligofluorenes can be enhanced by extending its conjugation length without affecting the emission wavelengths. Importantly, the three-photon absorption cross-section enhances significantly up to 2.48×10^{-78} cm^6 s^2 in the femtosecond regime, and the lasing efficiency increases parabolically with the conjugation length but without changing the lasing emission wavelength. Our findings open a new avenue to design highly efficient multiphoton absorption molecules for photoluminescence and lasing as well as a novel series of organic molecules that can be used in NLO applications and fundamental study.



p-PhN-OF(n)-TAZ, n = 2-4

Figure 1. Molecular structure of diphenylamino and 1,2,4-triazole end-capped π-conjugated oligofluorenes.

Table 1. Summaries of Physical Properties of *p*-PhN-OF(*n*)-TAZ

n	$\lambda_{\max}$[a] (nm) ε ($\times 10^4$/M^{-1} cm^{-1})	$\lambda^{\text{em}}_{\max}$[a,b] (nm)	Φ[a,c]	σ_2[d] (GM)	σ_3[e] (cm^6 s^2)	T_{dec}[f] (°C)
2	375 (8.02)	423	0.89	45	1.82×10^{-80}	484
3	376 (11.2)	423	0.86	57	2.66×10^{-79}	446
4	378 (15.4)	422	0.89	57	2.48×10^{-78}	454

[a] Measured in toluene. [b] Excited at the absorption maxima. [c] Using quinine sulfate monohydrate ($\Phi_{350} = 0.58$) as a standard. [d] σ_2 were determined by two-photon-induced fluorescence method using 800 nm femtosecond laser pulses with rhodamine 6G as a standard. [e] σ_3 were determined by optical limiting method using 1.3 μm femtosecond laser pulses. [f] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N$_2$.

To enhance the polarizability of a molecule, a donor−acceptor structure motif (D−π-A) using oligofluorenes (OF) as a π-conjugated core endcapped with the electron-donating diphenylamino group and the unconventionally employed electron-deficient 1,2,4-triazole (TAZ) derivatives as an acceptor was designed and synthesized for multiphoton absorption investigation. Our previously established convergent approach was adapted;[17] diphenylamino and 1,2,4,-triazole endcapped oligofluorenes, *p*-PhN-OF(*n*)-TAZ, where $n = 2-4$, were synthesized in good yields (Scheme S1 in Supporting Information). In general, palladium catalyzed Suzuki cross-coupling of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid[18] and 1,2,4,-triazole-substituted oligofluorenyl halide was used as a key step to construct the oligomers. All the newly synthesized oligofluorenes were fully characterized with ^{1}H NMR, ^{13}C NMR, MALDI-TOF HRMS, and elemental analysis and found to be in good agreement with their structures. (see Supporting Information)

The linear and nonlinear optical properties of these donor−acceptor oligofluorenes in toluene are summarized in Table 1. Although the absorption and emission maxima show a tendency of saturation with an increase in conjugation length, the molar absorptivity enhances significantly (Figure S1) and the fluorescence quantum yields remain very high (>85%). Interestingly, these oligofluorenes exhibit not only two-photon up-converted photoluminescence (PL) at 800 nm femtosecond laser pulses but also strong three-photon up-converted PL excited at near-infrared. Remarkably, very large three-photon absorption cross-sections in the femtosecond regime up to 2.48×10^{-78} cm^6 s^2 were determined by an optical limiting method, and these are among the highest values measured so far,[19] highlighting the potential of the materials for three-photon absorption applications. The two-photon and three-photon excited PL spectral characteristics are very similar to those

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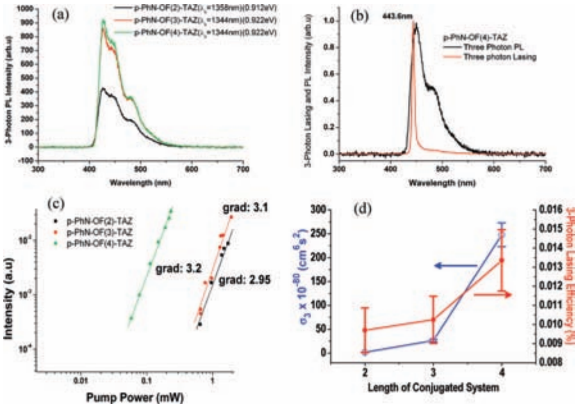

Figure 2. (a) Three-photon upconversion photoluminescence of oligofluorenes. The excitation wavelengths (energies) are optimized for the excitation. (b) Three-photon upconversion photoluminescence and lasing spectra of *p*-PhN-OF(4)-TAZ. (c) Plots of the lasing intensities of *p*-PhN-OF(n)-TAZ as function of pump power. (d) Plots of three-photon upconversion absorption cross-section and efficiency dependence of the length of the conjugation system.

of one-photon excited counterparts indicating that their emission energy levels are very similar. All the oligomers exhibit high thermal stability with decomposition temperatures >446 °C under nitrogen as analyzed by TGA which is a prerequisite for high-energy laser pumping.

Upon pumping with near-infrared femtosecond laser pulses, these oligomers exhibit remarkably multiphoton excited blue lasing. Consistent to the PL spectra, the two-photon excited lasing spectra of all the oligofluorenes were near-identical. Although the two-photon upconversion at 800 nm is not an optimum excitation wavelength for these oligomers, the lasing peaks are narrow, *p*-PhN-OF(2)-TAZ at 446 nm, *p*-PhN-OF(3)-TAZ at 450 nm, and *p*-PhN-OF(4)-TAZ at 448 nm with fwhm of 12.0 nm, 11.0 nm, and 12.0 nm, respectively, as compared to the PL peak at 427 nm with fwhm of 65 nm (Figure S2). It is worthy mentioning that nonconjugated diphenylamino and 1,2,4-triazole endcapped oligofluorenes i.e. *m*-PhN-OF(3)-TAZ can exhibit two-photon excited PL but not lasing phenomenon.

Figure 2a shows the PL spectra of the three-photon upconversion with the optimum excitation wavelength (λ_x) for each oligomers. All three PL spectra have near-identical shapes which are the same as those of two-photon upconversion PL. It is noted that *p*-PhN-OF(2)-TAZ has significantly less intensity than *p*-PhN-OF(3)-TAZ and *p*-PhN-OF(4)-TAZ, which have similar intensity. The three-photon upconversion lasing of *p*-PhN-OF(*n*)-TAZs is shown in Figure S3 and Figure 2b and for comparison its respective PL spectra was also included. The optimized fwhm of the three lasing spectra are 5.3 nm for *p*-PhN-OF(*n*)-TAZ, $n = 2$ and 3, and 5.6 nm for *p*-PhN-OF(4)-TAZ, respectively. They are the narrowest fwhm reported for three-photon excited lasing so far. The lasing peaks are in the deep blue visible region of 443−444 nm. The gradients of the lasing intensity as a function of pump power are about 3, confirming that the observed lasing is three-photon upconversion (Figure 2c). It is also shown that *p*-PhN-OF(4)-TAZ's threshold pump power is considerably smaller than the other counterparts.

It is important to note that both PL and lasing spectra for two-photon and three-photon upconversion are essentially the same among the three oligofluorenes. There is only a small shift of the peak wavelengths of no more than 1−2 nm from the three homologues oligomers. This implies that the emission energy originates from the same energy level/state for these oligomers which is independent of the conjugation length. Endcapping of diphenylamino and 1,2,4-triazole onto oligofluorene cores constitutes a D−π-A structural motif creating a strong dipole moment. As the dipole strength is a function of the distance between the two charges, it will increase with the increase in the conjugation length. The NLO effect such as multiphoton excitation is parabolically proportional to the polarization viz. dipole;[19] therefore, it is anticipated that upconversion efficiency will reflect this relationship. We derived the upconversion efficiency for the three-photon excitation and observed that it is parabolic with the conjugation length (Figure 2d). Such an observed increased in upconversion is attributed to the enhancement of polarization through extending the distance between two charges i.e. conjugation length.

In conclusion, efficient two-photon and three-photon excited photoluminescence and lasing have been demonstrated by pumping with near-infrared femtosecond lasers on a novel series of diphenylamino and 1,2,4-triazole endcapped π-conjugated oligofluorenes. In particular, the emission is in the deep blue region, and the three-photon excited lasing shows one of the narrowest fwhm recorded. It was also shown that the NLO effect increased parabolically with the conjugation length but without shifting the emission wavelength. This demonstrates that varying the length of the conjugated system is a very effective way to tailor an OF-based NLO device for deep blue application. Our findings open a new avenue to design highly efficient multiphoton absorption molecules for photoluminescence and lasing as well as provide a novel series of organic molecules that can be used in NLO applications and fundamental study.

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Supporting Information Available: Synthesis and experimental details, characterization data and optical spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dvornikov, A. S.; Rentzepis, P. M. *Opt. Commun.* **1995**, *119*, 341.
(2) Strickler, J. H.; Webb, W. W. *Opt. Lett.* **1991**, *16*, 1780.
(3) Polyzos, I.; Tsigaridas, G.; Fakis, M.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *Chem. Phys. Lett.* **2003**, *369*, 264.
(4) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.
(5) Kawata, S.; Sun, H. B.; Tanaka, T.; Takada, K. *Nature* **2001**, *412*, 697.
(6) Wang, I.; Bouriau, M.; Baldeck, P. L.; Martineau, C.; Andraud, C. *Opt. Lett.* **2000**, *27*, 1348.
(7) Lemercier, G.; Mulatier, J.-C.; Martineau, C.; Anémian, R.; Andraud, C.; Wang, I.; Stéphan, O.; Amari, N.; Baldeck, P. C. R. *Chimie* **2005**, *8*, 1308.
(8) Denk, W. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 6629.
(9) Liu, J.; Zhao, Y. W.; Zhao, J. Q. A.; Xia, D.; Jiang, L. J.; Wu, S.; Ma, L.; Dong, Y. Q.; Gu, Y. H. *J. Photochem. Photobiol. B* **2002**, *68*, 156.
(10) Meng, F. Q.; Nickel, E.; Drobizhev, M.; Kruk, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Spanger, C. W. *Abstr. Pap. Am. Chem. Soc.* **2003**, *226*, U503.
(11) He, G. S.; Zhao, C. F.; Bhawalker, J. D.; Prasad, P. N. *Appl. Phys. Lett.* **1995**, *67*, 3703.
(12) He, G. S.; Yuan, L.; Cui, Y.; Li, M.; Prasad, P. N. *J. Appl. Phys.* **1997**, *81*, 2529.
(13) He, G. S.; Markowicz, P. P.; Lin, T.-C.; Prasad, P. N. *Nature* **2002**, *415*, 767.
(14) (a) Wegmann, G.; Giessen, H.; Hertel, D.; Mahrt, R. F. *Solid State Commun.* **1997**, *104*, 759. (b) Kallinger, C.; Hilmer, M.; Haugeneder, A.; Perner, M.; Spirkl, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Müllen, K.; Gombert, A.; Wittwer, V. *Adv. Mater.* **1998**, *10*, 920. (c) Schneider, D.; Rabe, T.; Riedl, T.; Dobbertin, T.; Werner, O.; Kröger, M.; Becker, E.; Johannes, H.-H.; Kowalsky, W.; Weimann, T.; Wang, J.; Hinze, P.; Gerhard, A.; Stössel, P.; Vestweber, H. *Appl. Phys. Lett.* **2004**, *84*, 4693.
(15) (a) Schneider, D.; Rabe, T.; Riedl, T.; Dobbertin, T.; Kröger, M.; Becker, E.; Johannes, H.-H.; Kowalsky, W. *Appl. Phys. Lett.* **2004**, *85*, 1659. (b) Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J.; Rabe, T.; Riedl, T.; Johannes, H. H.; Kowalsky, W.; Wang, J.; Weimann, T.; Hinze, P. *Appl. Phys. Lett.* **2005**, *87*, 161103. (b) Karnutsch, C.; Gyrtner, C.; Haug, V.; Lemmer, U.; Farrell, T.; Nehls, B. S.; Scherf, U.; Wang, J.; Weimann, T.; Heliotis, G.; Pflumm, C.; deMello, J. C.; Bradley, D. D. C. *Appl. Phys. Lett.* **2006**, *89*, 201108.
(16) Bauer, C.; Schnabel, B.; Kley, E.-B.; Scherf, U.; Giessen, H.; Mahrt, R. F. *Adv. Mater.* **2002**, *14*, 673.
(17) (a) Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. *Chem.—Eur. J.* **2005**, *11*, 3285. (b) Gao, Z. Q.; Li, Z. H.; Xia, P. F.; Wong, M. S.; Cheah, K. W.; Chen, C. H. *Adv. Funct. Mater.* **2007**, *17*, 3194.
(18) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Org. Lett.* **2006**, *8*, 4271.
(19) Suo, Z.; Drobizhev, M.; Spangler, C. W.; Christensson, N.; Rebane, A. *Org. Lett.* **2005**, *7*, 4807.
(20) Shen, Y. R. *The Principles of Non-linear Optics*; John Wiley & Sons: Singapore, 1991.

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