Novel fluorophore based on a multi-substituted olefin skeleton with enhanced three-photon absorption in the femtosecond regime†

Tzu-Chau Lin,*[a] Qingdong Zheng,[b] Chang-Yu Chen,[a] Guang S. He,[b] Wei-Je Huang,[a]
Aleksandr I. Ryasnyanskiy[b] and Paras N. Prasad[b]

Received (in Cambridge, UK) 5th September 2007, Accepted 31st October 2007
First published as an Advance Article on the web 8th November 2007
DOI: 10.1039/b713656k

A new multipolar fluorophore based on a multi-substituted olefin skeleton that possesses strong three-photon absorption and optical-limiting properties in the femtosecond regime has been designed and synthesized; this archetype suggests a new strategy to further optimize molecular structures toward enhanced nonlinear absorptivities based on known materials.

In the past fifteen years, two-photon absorption (2PA) has attracted significant attention due to its variety of potential applications in the emerging field of photonics and biophotonics including optical power limiting,[1] 3D data storage,[2] frequency up-converted lasing,[3] 3-D microfabrication,[4] noninvasive bio-imaging/tracking,[5] and two-photon photodynamic therapy.[6] With the experience gained from the investigation of two-photon technologies, several efforts have recently started in studying materials with various symmetries that possess three-photon absorption (3PA).[7–9] The 3PA process offers an intriguing possibility for bio-imaging applications because a longer excitation wavelength in the near infrared region can be used, thus the scattered light losses and undesirable linear absorption within the living organism can be greatly reduced. Moreover, the intrinsic cubic dependence on the local optical intensity of the 3PA process affords a superior spatial confinement so that a higher contrast and spatial resolution in imaging can consequently be achieved. On the other hand, this higher order nonlinear absorption process can also provide a much better optical-limiting performance over a broader spectral region even under the same nonlinear transmission.[10] So far, enormous strides have been made in understanding the relationship between molecular structure and its 2PA property by investigating various compounds with different archetypes including quasi-linear,[11] multi-branched,[12] and dendritic[13] geometries. However, comparatively fewer efforts have been addressed in realizing of how molecular structure connects to 3PA efficiency.[7,8,9d,e] Nevertheless, it has been suggested that the judicious control of intramolecular charge-transfer efficiency[7b,c] and/or the effective size of the π-conjugation domain[8] through molecular design are crucial to promote the 3PA. Here, we present a new model fluorophore (**2**) built from multi-substituted olefin moieties and the initial findings of its enhanced 3PA and 3PA-based optical power limiting properties in the femtosecond regime.

The chemical structures and synthetic routes of the model chromophore **2** and the reference analogue (**1**) in the present work are illustrated in Fig. 1 and Scheme 1, respectively. The skeleton of the reference compound **1** is simply a three-branched dye structure with an electron-donor (*i.e.* triphenylamine) in the center and three diphenylaminofluorenyl moieties extended outward from it, whereas the scaffold of compound **2** is constructed by the same central electron-donor, which has six diphenylaminofluorenyl units at peripheral positions to form a six-branched dendritic structure. Hence the overall structure of compound **2** can be seen as attaching three additional branches to compound **1**. Compared to the reference compound **1**, the multi-substituted-olefin-based structure **2** is expected to show a larger multipolar character and increased effective π-electron number, which may lead to promoted nonlinear absorptivities.[14] The reference compound **1** was synthesized in 75% yield *via* a three-fold Heck reaction between 2-bromo-7-diphenylaminofluorene **3** and a trivinyl derivative of triphenylamine **4** (Scheme 1). Differently, the synthesis of compound **2** was accomplished by taking advantage of a recently developed one-pot catalytic reaction which integrates

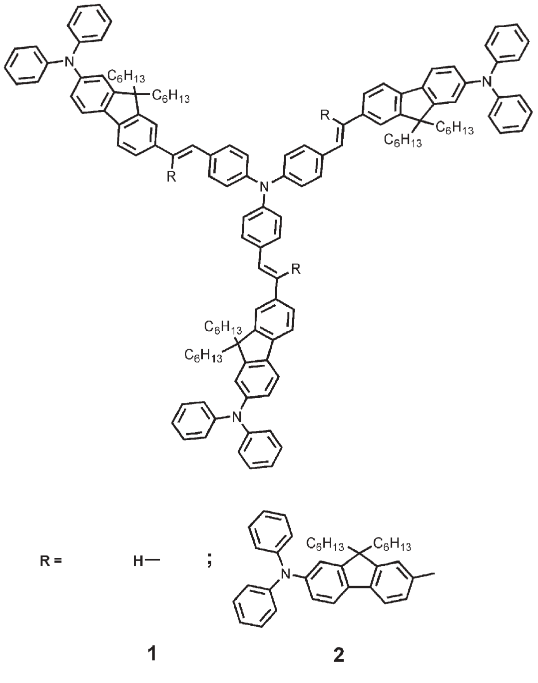
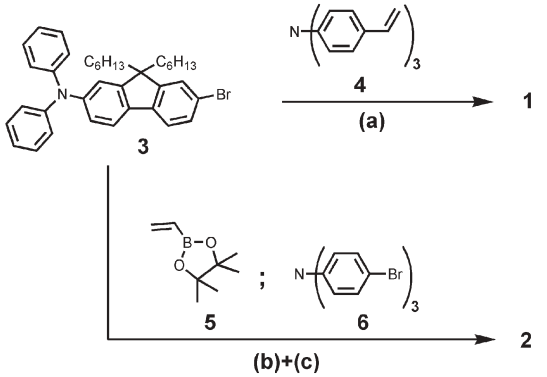


Fig. 1 Chemical structures of the studied model fluorophores.

---

[a] *Photonic Materials Research Laboratory, Department of Chemistry, National Central University, Jhong-Li, 32001, Taiwan*
E-mail: tclin@ncu.edu.tw
[b] *Institute for Lasers, Photonics and Biophotonics, State University of New York at Buffalo, Buffalo, NY, 14260-3000, USA*

† Electronic supplementary information (ESI) available: Experimental section and basis of nonlinear optical property characterizations. See DOI: 10.1039/b713656k



Scheme 1 Synthetic routes for the studied compounds **1** and **2**. *Reagents and conditions*: (a) Heck reaction: **3** (3.3 equiv.), **4** (1 equiv.), Pd(OAc)$_2$ (0.06 equiv.), P(*o*-tolyl)$_3$ (0.36 equiv.) in NEt$_3$–MeCN, 110 °C, 36 h (75%); (b) + (c) integrated one-pot catalytic reaction according to ref. 15: **3** (2 equiv.), **5** (1 equiv.), Pd[P(*t*-Bu)$_3$]$_2$ (0.05 equiv.), *i*-Pr$_2$NH (4 equiv.) in toluene, 90 °C, 24 h then addition of **6** (0.25 equiv.), NaOH (10 equiv), H$_2$O (8 equiv.), reflux, 24 h (overall yield ~45%).

the Mizoroki–Heck and cross-coupling reactions (MHR and CCR).[15] Using compound **3**, vinylboronate ester **5** and a tribromo derivative of triphenylamine **6** as the major synthons, compound **2** was obtained in *ca.* 45% overall yield. Compounds **3**, **4** and **6** were prepared by following the established methods as described in the ESI.†

Fig. 2 presents the absorption and fluorescence spectra of the studied dye molecules in chloroform. Both of these two chromophores show intense absorption around 400 nm. The shape and spectral position of their absorption bands are almost identical, but interestingly, the absorption intensity of the six-branched fluorophore (**2**) is about twice that of the three-branched analogue (**1**). This intriguing feature may imply a design approach to enhance molecular nonlinear absorption without shifting the major absorption band, which could be very useful for some particular applications when large multi-photon absorbing strength in a specific spectral region is required. Fig. 3 depicts the 3PA-induced fluorescence spectrum of compound **2** and the inset curve validates that the 3PA process is responsible for the observed upconversion emission. The 3PA cross-section values at several wavelengths of the studied chromophores were initially probed *via* the nonlinear transmission technique utilizing femtosecond pulses (see ESI†). Table 1 collects the preliminary photophysical characteristics of these two fluorophores in chloroform. Although the 3PA spectra of these two chromophores are not entirely revealed at the present stage (such work is being undertaken), the comparably strong 3PA observed from compound **2** in the NIR region indicates that this highly-branched structure with doubled peripheral-branches compared to its octupolar analogue (**1**) might provide an access for molecular structural optimization toward enhanced 3PA.

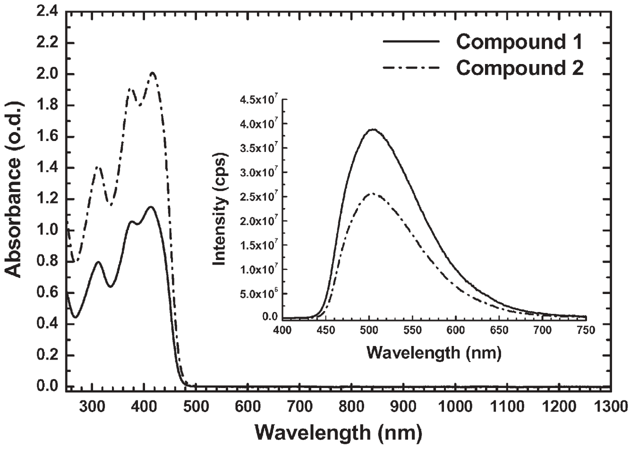


Fig. 2 Linear absorption and fluorescence spectra (see inset) of compounds **1** and **2** in solution (1 × 10^{-5} M in chloroform).

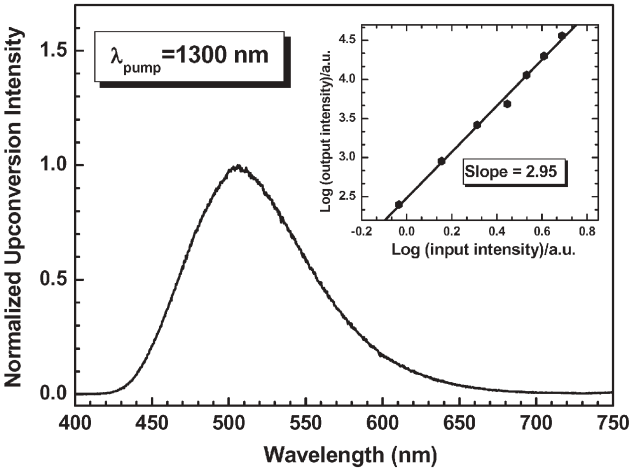


Fig. 3 Three-photon excited upconversion emission spectra of fluorophore **2** (5 × 10^{-3} M in CHCl$_3$). Inset, power dependence of the 3PA-excited upconversion emission intensity on the input intensity.

The 3PA-based optical power limiting performance of the model chromophore **2** was also evaluated in the femtosecond time domain using 1300 nm as the working wavelength for this experiment and the result is illustrated in Fig. 4. It is well known that an ideal optical-limiter is expected to show an intensity-dependent transmission feature so that the output intensity is always below a certain maximum value, which makes optical-limiters useful for protecting human eyes and sensors against damaging sources of light. Besides, this power limiting phenomenon is also important for optical dynamic range compression in optical signal processing and nonlinear ultra-fast filtering of optical fiber signals. Among the existing nonlinear processes, using multi-photon absorption for power-suppression has been pointed out as one of the effective tools against the dangers of frequency-agile/ultra-fast laser pulses.[16] As presented in Fig. 4, one can see that the input–output curve starts to deviate from linear transmission (diagonal dashed-line) at an energy level of ~0.2 μJ, and rapidly approaches a plateau while the pumping energy levels levels up to ~1.0 μJ. More specifically, when the input energy is increased from ~0.2 to ~3.4 μJ (~17-fold increase), the transmitted output only shifts from ~0.2 to 1.2 μJ (~6-fold increase), which fits the theoretically predicted optical-limiting behavior based on 3PA.

In conclusion, we have synthesized a new conjugated multipolar dye molecule with six branches attached to a central electron-donor unit *via* a catalytic reaction protocol. Current photophysical properties and the efficient 3PA-based optical-limiting performance in femtosecond regime observed from this model

Table 1 Photophysical properties of compounds **1** and **2** in chloroform

	$\lambda_{\max}^{1PA\,a,b}$/nm	$\varepsilon_{\max}/10^5$ M^{-1} cm^{-1}	$\lambda_{\max}^{1PA-FL\,b,c}$/nm	$\sigma^{3PA\ d}/10^{-24}$ cm^6 GW^{-2}			$\Phi_F{}^e$	$N_e{}^f$
				1217 nm	1300 nm	1445 nm		
1	413	1.15	504	13.4 (±15%)	17.1 (±15%)	4.7 (±15%)	0.98	37.6
2	417	2.01	505	21.0 (±15%)	22.1 (±15%)	7.3 (±15%)	0.45	59.2

[a] 1PA stands for one-photon absorption. [b] The concentration was 1 × 10^{-5} M. [c] 1PA-FL stands for 1PA-induced fluorescence. [d] The concentration was 5 × 10^{-3} M for 3PA cross-section measurements; experimental uncertainty ±15%. [e] Fluorescence quantum efficiency at room temperature was determined with coumarin 153 (Φ_F = 0.38) as the reference.[17] [f] Effective number of π-electrons.[14b]

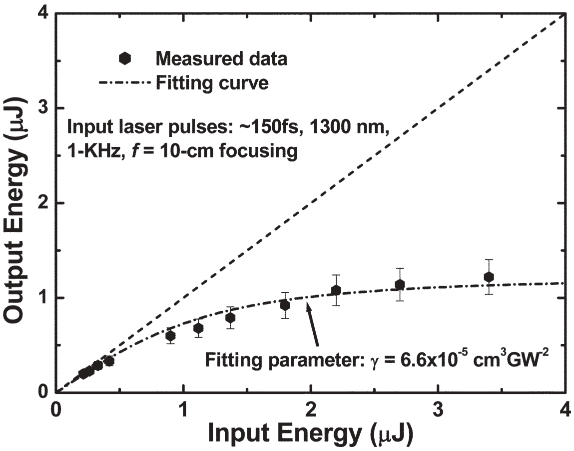


Fig. 4 Measured output energy *vs.* input energy of 1300 nm laser pulses based on a 1-cm path solution sample of compound **2** in $CHCl_3$ at 0.04 M. The dash-dotted curve is the theoretical data with a best-fit parameter of $\gamma = 6.6 \times 10^{-5}$ cm^3 GW^{-2}.

compound indicate that this structural motif may offer a new approach in molecular design to optimize chromophore structures with promoted nonlinear absorptivities in particular spectral regions based on the vast existing two- and three-photon-active materials.

T.-C. Lin acknowledges the financial support from the National Science Council (NSC), Taiwan (grant No. NSC 95-2113-M-008-013-MY2). Q. Zheng, G. S. He, A. I. Ryasnyanskiy and P. N. Prasad wish to acknowledge the financial support from the Chemistry and Life Sciences Directorate of the Air Force Office of Scientific Research (AFOSR) and in part from the John R. Oishei Foundation.

Notes and references

1 (*a*) J. B. Ehrlich, X. L. Wu, I.-Y. S. Lee, Z.-Y. Hu, H. Rockel, S. R. Marder and J. W. Perry, *Opt. Lett.*, 1997, **22**, 1843; (*b*) G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt and A. G. Dillard, *Opt. Lett.*, 1995, **20**, 435.

2 (*a*) D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843; (*b*) J. H. Strickler and W. W. Webb, *Opt. Lett.*, 1991, **16**, 1780.

3 (*a*) A. Abbotto, L. Beverina, R. Bozio, S. Bradamante, C. Ferrante, G. A. Pagani and R. Signorini, *Adv. Mater.*, 2000, **12**, 1963; (*b*) G. S. He, C. F. Zhao, J. D. Bhawalkar and P. N. Prasad, *Appl. Phys. Lett.*, 1995, **67**, 3703.

4 (*a*) B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Rockel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51; (*b*) W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry and S. R. Marder, *Science*, 2002, **296**, 1106.

5 (*a*) W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73; (*b*) T. Gura, *Science*, 1997, **276**, 1988; (*c*) X. Wang, L. J. Krebs, M. Al-Nuri, H. E. Pudavar, S. Ghosal, C. Liebow, A. A. Nagy, A. V. Schally and P. N. Prasad, *Proc. Natl. Acad. Sci. USA*, 1999, **96**, 11081; (*d*) L. Levy, Y. Sahoo, K.-S. Kim, E. J. Bergey and P. N. Prasad, *Chem. Mater.*, 2002, **14**, 3715.

6 J. D. Bhawalkar, N. D. Kumar, C. F. Zhao and P. N. Prasad, *J. Clin. Laser Med. Surg.*, 1997, **15**, 201.

7 (*a*) M. Samoc, J. P. Morrall, G. T. Dalton, M. P. Cifuentes and M. G. Humphrey, *Angew. Chem., Int. Ed.*, 2007, **46**, 731; (*b*) F. E. Hernández, K. D. Belfield and I. Cohanoschi, *Chem. Phys. Lett.*, 2004, **391**, 22; (*c*) I. Cohanoschi, K. D. Belfield and F. E. Hernández, *Chem. Phys. Lett.*, 2005, **406**, 462; (*d*) I. Cohanoschi, K. D. Belfield, C. Toro, S. Yao and F. E. Hernández, *J. Chem. Phys.*, 2006, **124**, 194707.

8 (*a*) M. Drobizhev, A. Karotki, M. Kruk, Y. Dzenis, A. Rebane, Z. Suo and C. W. Spangler, *J. Phys. Chem. B*, 2004, **108**, 4221; (*b*) Z. Suo, M. Drobizhev, C. W. Spangler, N. Christensson and A. Rebane, *Org. Lett.*, 2005, **7**, 4807; (*c*) M. Drobizhev, A. Rebane, Z. Suo and C. W. Spangler, *J. Lumin.*, 2005, **111**, 291.

9 (*a*) G. S. He, P. P. Markowicz, T.-C. Lin and P. N. Prasad, *Nature*, 2002, **415**, 767; (*b*) Q. Zheng, G. S. He, C. Lu and P. N. Prasad, *J. Mater. Chem.*, 2005, **15**, 3488; (*c*) Q. Zheng, G. S. He, A. Baev and P. N. Prasad, *J. Phys. Chem. B*, 2006, **110**, 14604; (*d*) T.-C. Lin, G. S. He, Q. Zheng and P. N. Prasad, *J. Mater. Chem.*, 2006, **16**, 2490.

10 (*a*) G. S. He and P. N. Prasad, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2003, **5211**, 1.

11 Selected examples: (*a*) B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.*, 1998, **10**, 1863; (*b*) M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653; (*c*) L. Ventelon, L. Moreaux, J. Mertzb and M. Blanchard-Desce, *Chem. Commun.*, 1999, 2055; (*d*) K. D. Belfield, A. R. Morales, B.-S. Kang, J. M. Hales, D. J. Hagan, E. W. Van Stryland, V. M. Chapela and J. Percino, *Chem. Mater.*, 2004, **16**, 4634; (*e*) T.-C. Lin, G. S. He, P. N. Prasad and L.-S. Tan, *J. Mater. Chem.*, 2004, **14**, 982.

12 Selected examples: (*a*) L. Porre's, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz and M. Blanchard-Desce, *Org. Lett.*, 2004, **6**, 47; (*b*) S. Yao and K. D. Belfield, *J. Org. Chem.*, 2005, **70**, 5126; (*c*) S.-J. Chung, K.-S. Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz and P. N. Prasad, *J. Phys. Chem. B*, 1999, **103**, 10741; (*d*) R. Kannan, G. S. He, T.-C. Lin and P. N. Prasad, *Chem. Mater.*, 2004, **16**, 185; (*e*) Y. Wang, G. S. He, P. N. Prasad and T. Goodson, III, 2005, **127**, 10126; (*f*) T.-C. Lin, G. S. He, Q. Zheng and P. N. Prasad, *J. Mater. Chem.*, 2006, **16**, 2490.

13 Selected examples: (*a*) Q. Zheng, G. S. He and P. N. Prasad, *Chem. Mater.*, 2005, **17**, 6004; (*b*) O. Varnavski, X. Yan, O. Mongin, M. Blanchard-Desce and T. Goodson, III, *J. Phys. Chem. C*, 2007, **111**, 149; (*c*) M. Drobizhev, A. Karotki, A. Rebane and C. W. Spangler, *Opt. Lett.*, 2001, **26**, 1081; (*d*) A. M. McDonagh, M. G. Humphrey, M. Samoc and B. Luther-Davies, *Organometallics*, 1999, **18**, 5195.

14 (*a*) M. Parent, O. Mongin, K. Kamada, C. Katan and M. Blanchard-Desce, *Chem. Commun.*, 2005, **15**, 2029; (*b*) M. G. Kuzyk, *J. Chem. Phys.*, 2003, **119**, 8327.

15 K. Itami, K. Tonogaki, Y. Ohashi and J.-i. Yoshida, *Org. Lett.*, 2004, **6**, 4093.

16 (*a*) C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013; (*b*) J. S. Shirk, *Opt. Photonics News*, 2000 April, 19.

17 (*a*) S. Fery-Forgues and D. Lavabre, *J. Chem. Educ.*, 1999, **76**, 1260; (*b*) G. A. Reynolds and K. H. Drexhage, *Opt. Commun.*, 1975, **13**, 222.