Tetrahedron Letters 50 (2009) 182-185

Contents lists available at ScienceDirect

**Tetrahedron Letters** 

journal homepage: www.elsevier.com/locate/tetlet



# Synthesis and two-photon properties of a multipolar chromophore containing indenofluorenyl units

Tzu-Chau Lin\*, Cheng-Sheng Hsu, Chia-Ling Hu, Yong-Fu Chen, Wei-Je Huang

Photonic Materials Research Laboratory, Department of Chemistry, National Central University, Jhong-Li 32001, Taiwan

## ARTICLE INFO

Article history: Received 26 August 2008 Revised 20 October 2008 Accepted 23 October 2008 Available online 29 October 2008

#### Keywords: Two-photon absorption Two-photon-excited fluorescence Indenofluorene Heck reaction

Over the past fifteen years, two-photon absorption (2PA) has attracted increasing attention due to its variety of potential applications in photonics and biophotonics including optical power limiting, 3-D data storage, frequency upconverted lasing, 3-D microfabrication, noninvasive bio-imaging/tracking, and twophoton photodynamic therapy.<sup>1</sup> To be of use in these applications, organic compounds that display strong 2PA within specific spectral region are consequently in great demand. The accumulated knowledge and experience based on enormous efforts devoted in understanding the connections between molecular structure and 2PA property has revealed that large 2PA can be achieved by judicious control of the intramolecular charge-transfer efficiency and/or effective size of Π-conjugation domain within a molecule.<sup>2-7</sup> Among the investigated structures, it has been experimentally shown that branched structures could lead to highly efficient multi-photon absorption<sup>3d,e,4,5d,6a,b,d,f,7e-g,8</sup> while maintaining linear transparency over wide spectral range.<sup>9</sup> On the other hand, branched skeleton offers an access to incorporate numbers of 2PA-enhancing parameters into a single dye system and this could be very desirable for material chemists from the aspect of molecular design since it is possible to optimize a single molecule that simultaneously combines various expected characteristics for different specific applications. Besides, branched skeletons are potential building blocks for constructing dendritic and/or supermolecular structures which are suggested as probable approaches to pursue fundamental limits of molecular 2PA.<sup>10</sup> In searching the correlation between structural parameters and nonlinear absorp-

# ABSTRACT

A new multipolar fluorophore derived from triphenylamine as the core with diphenylaminoindenofluorenyl moieties incorporated at the peripheral positions has been synthesized and experimentally shown to possess strong two-photon absorptivities in near-IR region and intense upconverted visible emission under the irradiation of femtosecond laser pulses.

© 2008 Elsevier Ltd. All rights reserved.

tion properties in conjugated systems, we have been interested in exploring the impact brought by potential 2PA-enhancing aromatic units with various structural/electronic properties when they are incorporated into the framework of a multi-branched chromophore. In this Letter, we present the synthesis of a new two-photon-active model chromophore (**2**) derived from triphenylamine and indenofluorene moieties as well as the initial investigations of its 2PA properties in the femtosecond time domain.

The chemical structure and the synthetic route of the studied model compound are illustrated in Scheme 1. The trigonal skeleton of this octupolar fluorophore is derived from the symmetric functionalization of an electron-donating core (i.e., triphenylamine) with three conjugated diphenylaminoindenofluorenyl branches extended outward from the center. The structure of indenofluorene can be virtually treated as an elongated version of fluorene that involves two fluorenyl units sharing one central benzene ring. Compared to fluorene, the scaffold of indenofluorene not only keeps the coplanar character but also extends the  $\pi$ -conjugation length, and additionally it provides extra sites to attach alkyl chains for the solubility improvement, which are the features desirable for 2PAactive dyes. On the other hand, it has been reported that organic structures comprising indenofluorenyl units either in polymeric<sup>11</sup> or small molecular<sup>12</sup> forms are highly fluorescent and this is very beneficial for the nonlinear optical property characterizations based on two-photon-excited fluorescence (2PEF) technique. All the above considerations lead to the strategy to incorporate indenofluorene moieties into the Π-framework of our model dye system. We have utilized vinylene units as the connecting spacers between the central core and the peripheral groups in order to ensure effective electronic conjugation between end groups and



<sup>\*</sup> Corresponding author. Tel.: +886 3 4227402; fax: +886 3 4227664. *E-mail address*: tclin@ncu.edu.tw (T.-C. Lin).

<sup>0040-4039/\$ -</sup> see front matter  $\odot$  2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2008.10.114



Scheme 1. Synthetic procedure for the studied model compound 2. Reagents and conditions: (a) Suzuki reaction: 2,5-dibromo-xylene (1 equiv), PhB(OH)<sub>2</sub> (2.2 equiv), K<sub>2</sub>CO<sub>3</sub> (5 equiv), Bu<sub>4</sub>NBr (2 equiv) in H<sub>2</sub>O, 70 °C, 2 h (98%); (b) 3 (1 equiv), KMnO<sub>4</sub> (4.7 equiv) in H<sub>2</sub>O-pyridine, reflux, 24 h (88%); (c) 4 (1 equiv) in H<sub>2</sub>SO<sub>4</sub>, rt, 4 h (82%); (d) 5 (1 equiv), KOH (24.8 equiv), N<sub>2</sub>H<sub>4</sub>+H<sub>2</sub>O (7 equiv) in diethylene glycol, 180 °C, 48 h (76%); (e) 6 (1 equiv), n-BuLi (6 equiv), C<sub>6</sub>H<sub>13</sub>Br (6 equiv) in THF, -78 °C, 12 h (70%); (f) 7 (1 equiv), BTMABr<sub>3</sub> (2.1 equiv), ZnCl<sub>2</sub> (2.3 equiv) in CH<sub>3</sub>COOH, 80 °C, 12 h (73%); (g) 8 (1 equiv), Ph<sub>2</sub>NH (1.1 equiv), NaO<sup>t</sup>Bu (4 equiv), Pd<sub>2</sub>(dba)<sub>3</sub> (0.01 equiv), BINAP (0.03 equiv) in tother, 80 °C, 24 h (54%); (h) Heck reaction: 9 (3.3 equiv), tris(4-vinylphenyl)amine (1 equiv), Pd(OAc)<sub>2</sub> (0.06 equiv), P(o-tolyl)<sub>3</sub> in NEt<sub>3</sub>-MeCN, 110 °C, 48 h (80%). (See ref. 17 for the chemical abbreviation.)

core moiety and allow multi-dimensional intramolecular charge transfer to take place within the chromophore. Hence, the overall molecular structure of the model compound (2) is expected to simultaneously possess several potential 2PA-enhancing characters including multi-directional intermolecular charge transfer between core and molecular termini, increased II-electron number, elongated coplanarity of the conjugation system, and improved solubilities. This model fluorophore was synthesized in 80% yield via a triple Heck-type coupling between 2-bromo-8-diphenylaminoindenofluorene 9 and tris(4-vinylphenyl)amine (Scheme 1). The framework of the key intermediate 9 was accomplished by preparing the indenofluorene unit (compound **6**) first<sup>12</sup> followed by a series of functionalization processes at the corresponding positions including alkylation at C6 and C12 positions to obtain 7, bromination at C2 and C8 positions to prepare **8**,<sup>13</sup> and finally a mono-amination to afford compound **9**.<sup>14</sup> For the purpose of comparison, a previously reported analogous dye molecule (1) bearing three diphenylaminofluorenyl units at the peripheral positions has been chosen as the reference compound in this work.<sup>15</sup>

Figure 1 presents the linear absorption and fluorescence spectra of the studied dye molecule (2) and the reference compound (1) in THF. Intense one-photon absorption (1PA) of both compounds was found around 400 nm (with  $\epsilon \sim \! 1.17 \times 10^5 \, cm^{-1} \, M^{-1}$  for 1 and  $\epsilon$  $\sim 1.95 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$  for **2**). The model chromophore (**2**) also exhibits strong two-photon-excited upconversion emission which can be readily observed through naked eyes even under the illumination of an  $\sim$ 790 nm unfocused femtosecond laser beam. Figure 2 illustrates the 2PA-induced fluorescence spectrum of compound 2 and the inset curve validates that the 2PA process is responsible for the detected upconversion emission. In order to explore and compare the dispersion of 2PA behaviors of these two dve molecules as a function of wavelength, we have conducted the degenerate twophoton-excited fluorescence (2PEF) measurement in the near-IR regime (700-900 nm) based on an experimental setup very similar to that reported by Xu and Webb<sup>16</sup> as depicted in Supplementary data (see Fig. S1). We have used Fluorescein (~80 µM in pH 11, NaOH solution) as the standard for this experiment. Figure 3 shows the measured degenerate two-photon absorption spectra of com-



Figure 1. Linear absorption and fluorescence spectra (see the inset) of compounds 1 and 2 in solution phase ( $1 \times 10^{-5}$  M in THF).

pound **1** and **2** in THF and the combined photophysical data are summarized in Table 1.

It is notable that the reference compound (1) exhibits relatively strong 2PA ( $\sigma_2 \ge 500$  GM) from 700 nm to 770 nm accompanied by a local maximum ( $\sigma_2 \sim 1620 \text{ GM}$ ) around 720 nm while the model fluorophore 2 possesses salient increment in the overall two-photon absorption within the entire investigated spectral region compared to compound 1, indicating that the expanded  $\pi$ -delocalization domain has positive contribution to the increased molecular 2PA. Also, indenofluorene appears to be a superior 2PA-promoting unit to fluorene in this triphenylamine-derived dye system. The dispersions of 2PA activities for these two chromophores are very similar within our current spectral detection range, that is, the 2PA cross-section values for both compounds approached to higher values at short excitation wavelength range and leveled down monotonically in the long excitation wavelength direction. The observed rising two-photon absorptivities in the short wavelength region implies that the two-photon allowed states with larger transition probabilities of these dye molecules are energetically positioned above their lowest one-photon allowed states.<sup>2a,b</sup> The dispersion of large two-photon activities in relatively wide near-IR spectral regime suggests that this model chromophore can be a potential broad-band optical power limiter when against ultra-short pulses. On the other hand, the medium-



**Figure 2.** Two-photon excited upconversion emission spectra of fluorophore **2** in THF at  $1\times 10^{-4}$  M. Inset, power dependence of the 2PA-induced upconversion emission intensity on the input intensity.



**Figure 3.** Measured degenerate two-photon absorption spectra of compounds **1** and **2** by 2PEF method in THF solution at  $1 \times 10^{-4}$  M (with experimental error  $\sim \pm 15\%$ ).

Table 1							
Photophysical	properties	of	compounds	1	and 2	<b>2</b> in	THF <sup>a</sup>

Compound	1PA-related optical properties				2PA-related optical properties <sup>g</sup>			$N_{\rm eff}^{i}$
	$\lambda_{MAX}^{1PA}$ b,c (nm)	$\log \epsilon_{MAX}^{d}$	$\lambda_{\rm MAX}^{\rm 1PA-FLe}$ (nm)	${\Phi_{\mathrm{F}}}^{\mathrm{f}}$	$\delta_2^{720nm}$ (GM) <sup>h</sup>	$\delta_2^{2\lambda_{1PA}} (GM)^h$	λ <sup>2PA-Fle</sup> (nm)	-
1 2	408 419	5.07 5.29	493 479	0.76 0.72	$\substack{\sim 1620\\\sim 5270}$	~180 ~510	494 482	37.6 47.4

<sup>a</sup> All photophysical data were obtained in THF solution.

<sup>b</sup> 1PA stands for one-photon absorption.

<sup>c</sup> The concentration was  $1 \times 10^{-5}$  M.

<sup>d</sup>  $\varepsilon_{MAX}$ : molar absorption coefficient.

<sup>e</sup> Spectral positions of 1PA-induced fluorescence emission maxima.

<sup>f</sup> Fluorescence quantum efficiency was determined with coumarin 153 as a reference.

The concentration was  $1 \times 10^{-4}$  M for 2PEF measurements.

<sup>h</sup> 2PA cross-section values at various wavelengths;  $1GM = 1 \times 10^{-50} \text{ cm}^4 \text{ s/pho-ton-molecule}$ 

Effective  $\pi$ -electron number.<sup>10</sup>

high quantum yield observed from this dye molecule also indicates that it could be an efficient frequency upconverter for the biophotonic applications such as two-photon-excited fluorescence microscopy. Additionally, from the viewpoint of practical applications, it might be interesting to explore the basic nonlinear photophysical properties of the model compound **2** in its solid state (e.g., in film configuration) and such work is under taken.

In summary, we have synthesized and investigated a novel multipolar chromophore with triphenylamine as the central core and diphenylaminoindenofluorene units as the peripheries. The large enhancement of 2PA observed from this fluorophore compared to the reference compound (1) implies that indenofluorene unit could be a useful 2PA-enhancer when correctly incorporated into a dye system. Furthermore, the strong 2PA that covers relatively wide spectral range in near-IR regime and intense 2PA-induced upconverted emission observed from this model compound make it a potential candidate for both broad-band optical limiter and frequency upconverter for various photonic and biophotonic applications.

### Acknowledgments

We acknowledge the financial support from National Science Council (NSC), Taiwan (Grant No. NSC 95-2113-M-008-013-MY2).

We also thank Professor Chao-Yi Tai and Dr. Sheng-Hsung Chang in the Department of Optics and Photonics, National Central University, Taiwan for their helpful assistance in part of photophysical property measurements.

# Supplementary data

The supplementary data includes detailed experimental procedures for optical property characterizations for model compounds and synthetic processes/full characterization data for compounds **2**, **7**, **8**, and **9**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.tetlet.2008.10.114.

### **References and notes**

- (a) Spangler, C. W. J. Mater. Chem. **1999**, 9, 2013–2020; (b) He, G. S.; Tan, L.-S.; Zheng, Q.; Prasad, P. N. Chem. Rev. **2008**, 108, 1245–1330; (c) Lin, T.-C.; Chung, S.-J.; Kim, K.-S.; Wang, X.; He, G. S.; Swiatkiewicz, J.; Pudavar, H. E.; Prasad, P. N. Adv. Polym. Sci. (Polymers for Photonics Applications II) **2003**, 161, 157–193.
- (a) Albota, M.; Beljonne, D.; Brédas, J.-L.; Ehrlich, J. É.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. Science **1998**, 281, 1653–1656; (b) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J.-L. J. Am. Chem. Soc. **2000**, 122, 9500–9510; (c) Chung, S.-J.; Rumi, M.; Alain, V.; Barlow, S.; Perry, J. W.; Marder, S. R. J. Am. Chem. Soc. **2005**, 127, 10844–10845; (d) Chung, S.-J.; Zheng, S.; Odani, T.; Beverina, L.; Fu, J.; Padilha, L. A.; Biesso, A.; Hales, J. M.; Zhan, X.; Schmidt, K.; Ye, A.; Zojer, E.; Barlow, S.; Hagan, D. J.; Stryland, E. W. V.; Yi, Y.; Shuai, Z.; Pagani, G. A.; Bredas, J.-L.; Perry, J. W.; Marder, S. R. J. Am. Chem. Soc. **2006**, 128, 14444–14445.
- (a) Ventelon, L.; Moreaux, L.; Mertzb, J.; Blanchard-Desce, M. Chem. Commun. 1999, 2055-2056; (b) Ventelon, L.; Moreaux, L.; Mertz, J.; Blanchard-Descec, M. Synth. Met. 2002, 127, 17-21; (c) Mongin, O.; Porre, L.; Moreaux, L.; Mertz, J.; Blanchard-Desce, M. Org. Lett. 2002, 4, 719-722; (d) Porres, L.; Katan, C.; Mongin, O.; Pons, T.; Mertz, J.; Blanchard-Desce, M. J. Mol. Struct. 2004, 704, 17-24; (e) Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. Org. Lett. 2004, 6, 47-50; (f) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porres, L.; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. J. Phys. Chem. A 2005, 109, 3024-3037; (g) Charlot, M.; Porres, L.; Entwistle, C. D.; Beeby, A.; Marder, T. B.; Blanchard-Desce, M. Phys. Chem. Chem. Phys. 2005, 7, 600-606; (h) Charlot, M.; Izard, N.; Mongin, O.; Riehl, D.; Blanchard-Desce, M. Chem. Phys. Lett. 2006, 417, 297-302; (i) Terenziani, F.; Droumaguet, C. L.; Katan, C.; Mongin, O.; Blanchard-Desce, M. ChemPhysChem 2007, 8, 723-734.
- (a) Drobizhev, M.; Karotki, A.; Rebane, A.; Spangler, C. W. Opt. Lett. 2001, 26, 1031–1033;
   (b) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Suo, Z.; Spangler, C. W. J. Phys. Chem. B 2003, 107, 7540–7543;
   (c) Drobizhev, M.;

Rebanea, A.; Suoc, Z.; Spangler, C. W. J. Lumin. **2005**, *111*, 291–305; (d) Drobizhev, M.; Meng, F.; Rebane, A.; Stepanenko, Y.; Nickel, E.; Spangler, C. W. J. Phys. Chem. B **2006**, *110*, 9802–9814.

- (a) Belfield, K. D.; Hagan, D. J.; Van Stryland, E. W.; Schafer, K. J.; Negres, R. A. Org. Lett. **1999**, *1*, 1575–1578; (b) Belfield, K. D.; Morales, A. R.; Hales, J. M.; Hagan, D. J.; Stryland, E. W. V.; Chapela, V. M.; Percino, J. Chem. Mater. **2004**, *16*, 2267–2273; (c) Belfield, K. D.; Morales, A. R.; Kang, B.-S.; Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Chapela, V. M.; Percino, J. Chem. Mater. **2004**, *16*, 4634–4641; (d) Yao, S.; Belfield, K. D.; *J. org. Chem.* **2005**, *70*, 5126–5132; (e) Morales, A. R.; Belfield, K. D.; Hales, J. M.; Stryland, E. W. V.; Hagan, D. J. Chem. Mater. **2006**, *18*, 4972–4980; (f) Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V. J. Phys. Chem. C **2008**, *112*, 5618–5622.
- (a) Wang, Y.; He, G. S.; Prasad, P. N.; Goodson T., III. 2005, 127, 10126–10129.;
   (b) Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R.; Hales, J. M.; Hagan, D. J.; Stryland, E. V.; Goodson, T., III J. Am. Chem. Soc. 2006, 128, 11840–11849; (c) Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T., III J. Am. Chem. Soc. 2006, 128, 13972–13973; (d) Ramakrishna, G.; Goodson, T., III J. Phys. Chem. A 2007, 111, 993–1000; (e) Bhaskar, A.; Ramakrishna, G.; Hagedorn, K.; Varnavski, O.; Mena-Osteritz, E.; Ba1uerle, P.; Goodson, T., III J. Phys. Chem. B 2007, 111, 946–954; (f) Varnavski, O.; Van, X.; Mongin, O.; Blanchard-Desce, M.; Goodson, T., III J. Phys. Chem. C 2007, 111, 149–162; (g) Williams-Harry, M.; Bhaskar, A.; Ramakrishna, G., ; Goodson, T., III; Imamura, M.; Mawatari, A.; Nakao, K.; Enozawa, H.; Nishinaga, T.; Iyoda, M. J. Am. Chem. Soc. 2008, 130, 3252–3253.
- (a) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. Chem. Mater. **1998**, *10*, 1863–1874; (b) Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L.-S. Chem. Mater. **2001**, *13*, 1890– 1904; (c) Kannan, R.; He, G. S.; Lin, T.-C.; Prasad, P. N.; Vaia, R. A.; Tan, L.-S. Chem. Mater. **2004**, *16*, 185–194; (d) Nguyen, K. A.; Rogers, J. E.; Slagle, J. E.; Day, P. N.; Kannan, R.; Tan, L.-S.; Fleitz, P. A.; Pachter, R. J. Phys. Chem. A **2006**, *110*, 13172–13182; (e) Chung, S.-J.; Kim, K.-S.; Lin, T.-C.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. J. Phys. Chem. B **1999**, *103*, 10741–10745; (f) Lin, T.-C.; He, G. S.; Zheng, Q.; Prasad, P. N. J. Mater. Chem. **2004**, *16*, 2490–2498.
- Suo, Z.; Drobizhev, M.; Spangler, C. W.; Christensson, N.; Rebane, A. Org. Lett. 2005, 7, 4807–4810.
- (a) Mongin, O.; Brunel, J.; Porres, L.; Blanchard-Desce, M. *Tetrahedron Lett.* 2003, 44, 2813–2816; (b) Mongin, O.; Porres, L.; Katan, C.; Pons, T.; Mertzb, J.; Blanchard-Desce, M. *Tetrahedron Lett.* 2003, 44, 8121–8125.
- 10. Kuzyk, M. G. J. Chem. Phys. 2003, 119, 8327-8334.
- 11. Stampfl, J.; Tasch, S.; Leising, G.; Scherf, U. Synth. Met. 1995, 71, 2125.
- 12. Merlet, S.; Birau, M.; Wang, Z. Y. Org. Lett. 2002, 4, 2157-2159.
- Kajigaeshi, S.; Kakinami, T.; Moriwaki, M.; Tanaka, T.; Fujisaki, S.; Okamoto, T. Bull. Chem. Soc. Jpn. **1989**, 62, 439–443.
- Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. J. Am. Chem. Soc. 1996, 118, 7215–7216.
   Lin, T.-C.; Zheng, Q.; Chen, C.-Y.; He, G. S.; Huang, W.-J.; Ryasnyanskiy, A. I.;
- Prasad, P. N. *Chem. Commun.* **2008**, 389–391. 16. Xu, C.; Webb, W. W. J. *Opt. Soc. Am. B* **1996**, *13*, 481–491.

phino)-1,1'-biphenyl; P(o-tolyl)<sub>3</sub>: tri-o-tolyl phosphine.

Xu, C., Webb, W. W. J. Opt. Soc. Ant. B 1596, 13, 461–451.
 Key for the chemical abbreviations: PhB(OH)<sub>2</sub>: phenylboronic acid; Bu<sub>4</sub>NBr: tetrabutylammonium bromide; n-BuLi: n-butyl lithium; BTMABr<sub>3</sub>: benzyltrime-thylammonium tribromide; NaO<sup>6</sup>Bu: sodium tert-butoxide; Pd<sub>2</sub>(dba)<sub>3</sub>: tris (dibenzylideneacetone)dipalladium(0); BINAP: rac-2.2'- bis(diphenylphos-