J|A|C|S
COMMUNICATIONS

# Trinaphthylamines as Robust Organic Materials for Two-Photon-Induced Fluorescence

Guillaume Bordeau,† Rémy Lartia,† Germain Metge,‡ Céline Fiorini-Debuisschert,‡ Fabrice Charra,‡
and Marie-Paule Teulade-Fichou*,†

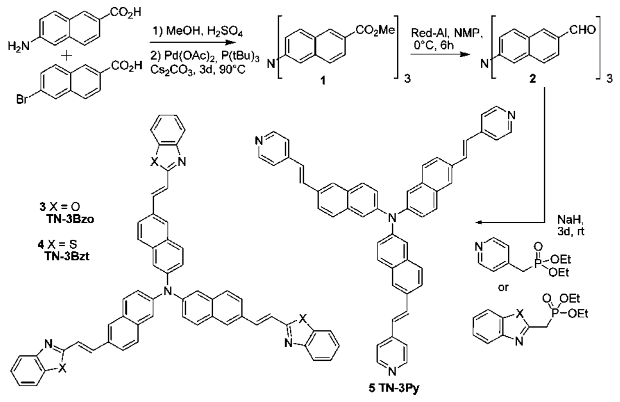
*Institut Curie, CNRS UMR-176, Centre Universitaire, 91405 Orsay Cedex, France, and CEA- Saclay, DSM/
DRECAM/SPCSI, 91191 Gif-sur-Yvette, France*

Received July 24, 2008; E-mail: marie-paule.teulade-fichou@curie.fr

Two-photon absorption (2PA) has recently attracted considerable interest due to its potential applications in a number of areas, including two-photon fluorescence imaging,[1] 3D optical data storage,[2] optical power limiting,[3] and photodynamic therapy.[4] A broad variety of donor−$\pi$-conjugated bridge−acceptor compounds of dipolar-,[5] quadripolar-,[6] and octupolar-[7]type has been studied. In particular acceptor-terminated triphenylamines (TP) have been shown to be excellent materials for 2PA[7] because of strong intramolecular charge-transfer (ICT), additional coherent coupling between branches, in the case of multibranched systems, resulting in a further increase of the 2PA cross-section.[6−8] TP is an electron-rich, propeller-shaped molecule with $C_3$ symmetry displaying an octupolar feature and which can be linked to different electron-withdrawing end groups via $\pi$-conjugated units. Many studies have explored this design, developing efficient fluorescent TP derivatives with high 2PA cross-sections.[7] In all these studies, the strength of the acceptor end groups and the size of the bridges were varied to increase the ICT. Comparatively, the reverse strategy, that is, structural variation of the $C_3$-symmetry core to enhance its electron-donating property, has never been considered presumably because of the lack of a synthetic pathway to other appropriate triarylamine cores. Hence we speculated that extending triphenyl to the trinaphthyl motif would strongly enrich the electron-donating property of the three-branched core. Herein, we would like to report on the simple synthesis and on the photophysical properties of three tris(2-naphthyl)amine derivatives (TN) $\pi$-conjugated with different acceptor groups. We show that switching from a classical TP core to a more electron-rich TN (displaying a larger electronic $\pi$-cloud) leads to a substantial increase in 2PA cross-section as compared to their TP counterparts. Additionally, to our knowledge, examples of trinaphthylamines are very scarce[9] and in particular tris(2-naphthyl)amines have never been reported.

The synthesis of the TN derivatives (Scheme 1) was straightforward (four steps) and efficient (30−37% overall yields). The commercially available 6-bromo-2-naphthoïc acid (100%) and 6-amino-2-naphthoïc acid (92%) were transformed to their ester derivatives and coupled via a Pd-catalyzed Buchwald−Hartwig to give **1** (79%). The subsequent ester reduction carried out via the classical two-step procedure (reduction to alcohol followed by smooth oxidation to aldehyde) led to an intractable mixture of under- and over-reduced products. Hence we developed an alternative one−step synthesis to the key trialdehyde intermediate **2**, via the concomitant triple reduction of the compound **1** with a modified Red-Al reagent[10] (74% yield). Then 4-pyridinyl, 2-benzothiazolyl, and 2-benzoxazolyl moieties were introduced via vinylation because these are efficient electron-withdrawing groups frequently incorporated into push−pull NLO materials.[11] This was achieved by Wittig−Horner reaction between the trialdehyde **2** and the corresponding phosphonate affording the three TN derivatives **TN-3BZo**, **TN-3Bzt**, and **TN-3Py** (60−73%).

***Scheme 1.*** Synthesis of the New Trinaphthylamine Derivatives



The photophysical properties of TN derivatives were studied in toluene and dichloromethane and the results are summarized in Table 1. All the TN compounds show a broad and intense absorption band ($\epsilon$ = 90 000−115 000 L·mol$^{-1}$·cm$^{-1}$) with maximum absorption wavelength between 400 and 440 nm slightly red-shifted compared to that of their TP counterparts[11] (Table 1). Importantly a strong increase of the one-photon absorption efficiency was observed (ca. 20−30%) in correlation with the increased $\pi$-conjugated surface. All compounds display high fluorescence quantum yields in dichloromethane ($0.5 < \Phi < 0.65$) and large Stokes shifts (95−125 nm, Table 1). These large Stokes shifts, that are important to avoid reabsorption, are close to those of the corresponding TP with a slight increase due to a red shift of the fluorescence. The

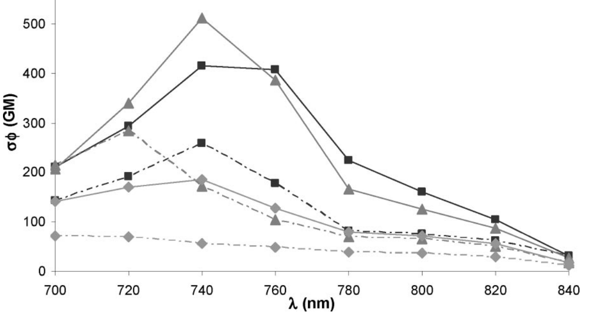


***Figure 1.*** Two-photon excitation spectra of compounds in $CH_2Cl_2$: Bzt series (■), Bzo series (▲), Py series (◇); **TN** (plain lines), **TP** (dashed lines). Values are average of three independent experiments.

---

† Institut Curie, CNRS UMR-176.
‡ CEA- Saclay, DSM/DRECAM/SPCSI.

10.1021/ja8055112 CCC: $40.75 © 2008 American Chemical Society

*Table 1.* 1PA and 2PA Photophysical Properties of TN and TP Derivatives

| compound | $\lambda_{abs}$ (nm) |  | $\epsilon^a$ (L.mol$^{-1}$.cm$^{-1}$) | $\lambda_{em}$ (nm) |  | $\Phi^{a,b}$ | 2PA $\sigma^a_{max}$ [$\lambda_{max}$] (GM) [nm] | $\sigma\Phi$ (GM) | $\sigma$/MW (GM·g$^{-1}$·mol) |
|---|---|---|---|---|---|---|---|---|---|
|  | toluene | $CH_2Cl_2$ |  | toluene | $CH_2Cl_2$ |  |  |  |  |
| *TN Series* |  |  |  |  |  |  |  |  |  |
| TN-3Py | 415 | 414 | 79400 | 465 | 528 | 0.58 | 320[740] | 185 | 0.45 |
| TN-3Bzt | 440 | 434 | 114900 | 485 | 559 | 0.65 | 640[740] | 415 | 0.73 |
| TN-3Bzo | 434 | 431 | 111100 | 478 | 542 | 0.63 | 810[740] | 510 | 0.98 |
| *TP Series* |  |  |  |  |  |  |  |  |  |
| TP-3Py | 402 | 406 | 59500 | 462 | 511 | 0.51 | 130[720] | 65 | 0.23 |
| TP-3Bzt | 435 | 432 | 97300 | 479 | 534 | 0.50 | 510[740] | 255 | 0.70 |
| TP-3Bzo | 431 | 424 | 89000 | 469 | 518 | 0.52 | 540[720] | 280 | 0.80 |

[a] Measurements were performed in $CH_2Cl_2$ [b] Fluorescence emission quantum yield, measured using quinine bisulphate in 1 N $H_2SO_4$ as a reference.

quantum yields are also enhanced by 20%, likely due to higher $\pi$-delocalization and additional rigidity. All the derivatives show a large bathochromism shift in their fluorescence emission along with the increase of the solvent polarity but no red shift of the absorption band. This solvatochromism behavior is characteristic of an internal charge transfer upon excitation[12] between the triarylamine core and peripheral acceptor groups. Moreover, this solvatochromism is more pronounced in the TN series than in the TP series, reflecting an increase of ICT (Table S1).

2PA spectra of the dyes were obtained after two-photon-induced fluorescence (TPIF) measurements, using a femtosecond Ti:sapphire laser source. The TPIF intensities of the samples were measured and compared with a reference solution of fluorescein, the ratio of the fluorescent signals enabling determination of the 2PA cross-section (Figure 1).[13]

Importantly, the three TN show high 2PA cross-sections that were strongly enhanced (up to 810 GM) as compared to that of the TP counterparts. Additionally, as a consequence of both enhancement of 2PA cross section and quantum yield, the TN derivatives exhibit a two to 3-fold increase of the action cross-section defined by the product of the 2PA cross-section and emission quantum yield ($\sigma\Phi$). This enhancement effect is modulated by the strength of the acceptor since it is particularly emphasized in the case of the weaker acceptor Py ($\sigma\Phi$ increasing from 65 to 185), whereas slightly attenuated for the Bzt and Bzo series (from 255−280 GM to 415−510 GM, respectively). This result is however difficult to rationalize given the dispersion inherent to measurements of 2PA cross sections.[14] Nonetheless the ranking order of the $\sigma\Phi$ values observed in the TN series is still reflecting the strength of the terminal acceptor (Py < Bzt ∼ Bzo). Altogether, these results fully validate our hypothesis that increasing the donor character of the triarylamine core leads to a stronger ICT.

Another way to increase 2PA cross section is to extend the $\pi$-bridge linking donor and acceptor groups, but this inevitably results in large-sized systems that may limit applications such as bioimaging. Interestingly, the high 2PA performances of the TN compounds are accompanied by only a slight increase in molecular weight (4 carbons/branch). To compare the 2PA performances of different series, the two-photon absorption/molecular weight ratio ($\sigma$/MW) is shown to be a relevant figure of merit.[7d] In this regard, our compounds fall in the range of the best large-sized 2PA chromophores reported to date[15] with a $\sigma$/MW ratio up to 0.98 GM·g$^{-1}$·mol for TN-3Bzo (Table 1).

In conclusion, we described an original new family of trinaphthylamine derivatives which are very efficient fluorophores for 2PA absorption. Their high 2PA cross-sections represent an interesting improvement as compared to the widely explored triphenylamine derivatives. Given the straightforward synthesis of the derivatizable trisformyl TN key intermediate **2** proposed herein, this work opens broad perspectives for new molecular design of fluorescent 2PA-organic materials based on the trinaphthylamine core.

**Acknowledgment.** This research was supported by MENRT (Ministère Education Nationale, Recherche et Technologie, Ph.D. fellowship to G.B.), C'nano IdF (Nanosciences Ile de France, Ph.D. fellowship to G.M.) and EU-FP6-NMP4-2003-505-669 (post doctoral fellowship to R.L.)

**Supporting Information Available:** Complete ref 6a,b. Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) (a) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73–76. (b) Xu, C.; Zipfel, W.; Shear, J. B.; Williams, R. M.; Webb, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10763–10768.
(2) (a) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843–845.
(3) Ehrlich, J. E.; Wu, X. L.; Lee, I.-Y. S.; Hu, Z.-Y.; Röckel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843–1845.
(4) Bhawalkar, J. D.; Kumar, N. D.; Zhao, C. F.; Prasad, P. N. *J. Clin. Laser Med. Surg.* **1997**, *15*, 201–204.
(5) (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) Abbotto, A.; Beverina, L.; Bozio, R.; Bradamante, S.; Ferrante, C.; Pagani, G. A.; Signorini, R. *Adv. Mater.* **2000**, *12*, 1963–1967.
(6) (a) Albota, M.; et al. *Science* **1998**, *281*, 1653–1656. (b) Zheng, S.; et al. *Chem. Mater.* **2007**, *19*, 432–442.
(7) (a) Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2004**, *6*, 47–50. (b) Lee, W.-H.; Lee, H.; Kim, J.-A.; Choi, J.-H.; Cho, M.; Jeon, S.-J.; Cho, B. R. *J. Am. Chem. Soc.* **2001**, *123*, 10658. (c) He, G. S.; Swiatkiewicz, J.; Jiang, Y.; Prasad, P. N.; Reinhardt, B. A.; Tan, L. S.; Kannan, R. *J. Phys. Chem. A* **2000**, *104*, 4805–4810. (d) 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.
(8) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Suo, Z.; Spangler, C. W. *J. Phys. Chem. B* **2003**, *107*, 7540–7543.
(9) Alameddine, B.; Savary, S.; Aebisher, O.; Jenny, T. A. *Synthesis* **2007**, *2*, 271–276, and patents cited herein.
(10) Hagiya, K.; Mitsui, S.; Taguchi, H. *Synthesis* **2003**, 823–828.
(11) (a) Allain, C.; Schmidt, F.; Lartia, R.; Bordeau, G.; Fiorini-Debuisschert, C.; Charra, F.; Tauc, P.; Teulade-Fichou, M.-P. *ChemBioChem* **2007**, *8*, 424–433. (b) Lartia, R.; Allain, C.; Bordeau, G.; Schmidt, F.; Fiorini-Debuisschert, C.; Charra, F.; Tauc, P.; Teulade-Fichou, M.-P. *J. Org. Chem.* **2008**, *73*, 1732–1744. (c) Nielsen, C. B.; Johnsen, M.; Arnbjerg, J.; Pittelkow, M.; McIlroy, S. P.; Ogilby, P. R.; Jorgensen, M. *J. Org. Chem.* **2005**, *70*, 7065–7079.
(12) Diwu, Z.; Zhang, C.; Klaubert, R. P.; Haughland, J. *J. Photochem. Photobiol., A* **2000**, *131*, 95–100.
(13) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481–491.
(14) Jha, P. C.; Wang, Y.; Agren, H. *Chemphyschem* **2008**, *9*, 111–116.
(15) (a) Yang, W. J.; Kim, D. Y.; Kim, C. H.; Jeong, M.-Y.; Lee, S. K.; Jeon, S.-J.; Cho, B. R. *Org. Lett.* **2004**, *6*, 1389–1392. (b) Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R.; Hales, J. M.; Hagan, D. J.; VanStryland, E.; Goodson, T. *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849.

JA8055112