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Switching High Two-Photon Efficiency: From 3,8,13-Substituted Triindole Derivatives to Their 2,7,12-Isomers

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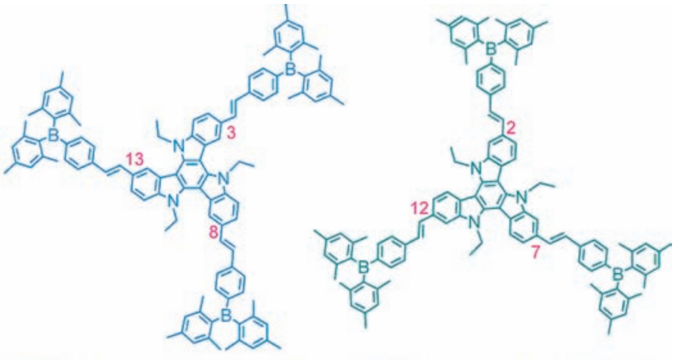
ABSTRACT



3-BET: Φδ = 0.33 × 2100 GM **2-BET**: Φδ = 0.40 × 2500 GM

Bridging the triindole core and triarylboryl acceptor by an ethenylene linker at the 3,8,13- or 2,7,12-position, the resultant 3-BET and 2-BET show two-photon absorption (TPA) cross sections of $\delta = 2100$ and 2500 GM (at 810 nm by femtosecond pulses in THF), respectively. The TPA enhancement of the 2,7,12-isomers is also found when comparing 3-BYT and 2-BYT ($\delta =$ 870 and 1900 GM) and 3-NET and 2-NET (36 and 400 GM).

Two-photon absorption (TPA), in which two photons are absorbed simultaneously by a molecule, was first predicted by Göppert-Mayer in the early 1930s.[1] Nowadays, TPA-based achievement covers wide fields in photophysics, photochemistry, and materials and life sciences, as has been summarized in several recent reviews.[2] In exploring new and better TPA chromophores, the C_3-symmetric octupolar motif proves to be a successful architecture[2−7] in addition to the well-established dipolar and quadrupolar models.

Triphenylamine,[3] *s*-triazine,[4] 1,3,5-tricyanobenzene,[5] triphenylbenzene,[6] and truxene[7] have been typically taken as the octupolar core, from which three π-conjugated arms are extended and acceptors (or donors) are end-capped for promoting intramolecular charge transfer (ICT). The large TPA cross section of these octupolar molecules may be interpreted in terms of the excitation model,[8] by which an octupole is treated as three individual dipoles with weak coupling between them.

Triindole is a highly π-conjugated planar molecule,[9] which resembles truxene. The replacement of three 5,10,15-C atoms of truxene by three N atoms endows the resultant triindole

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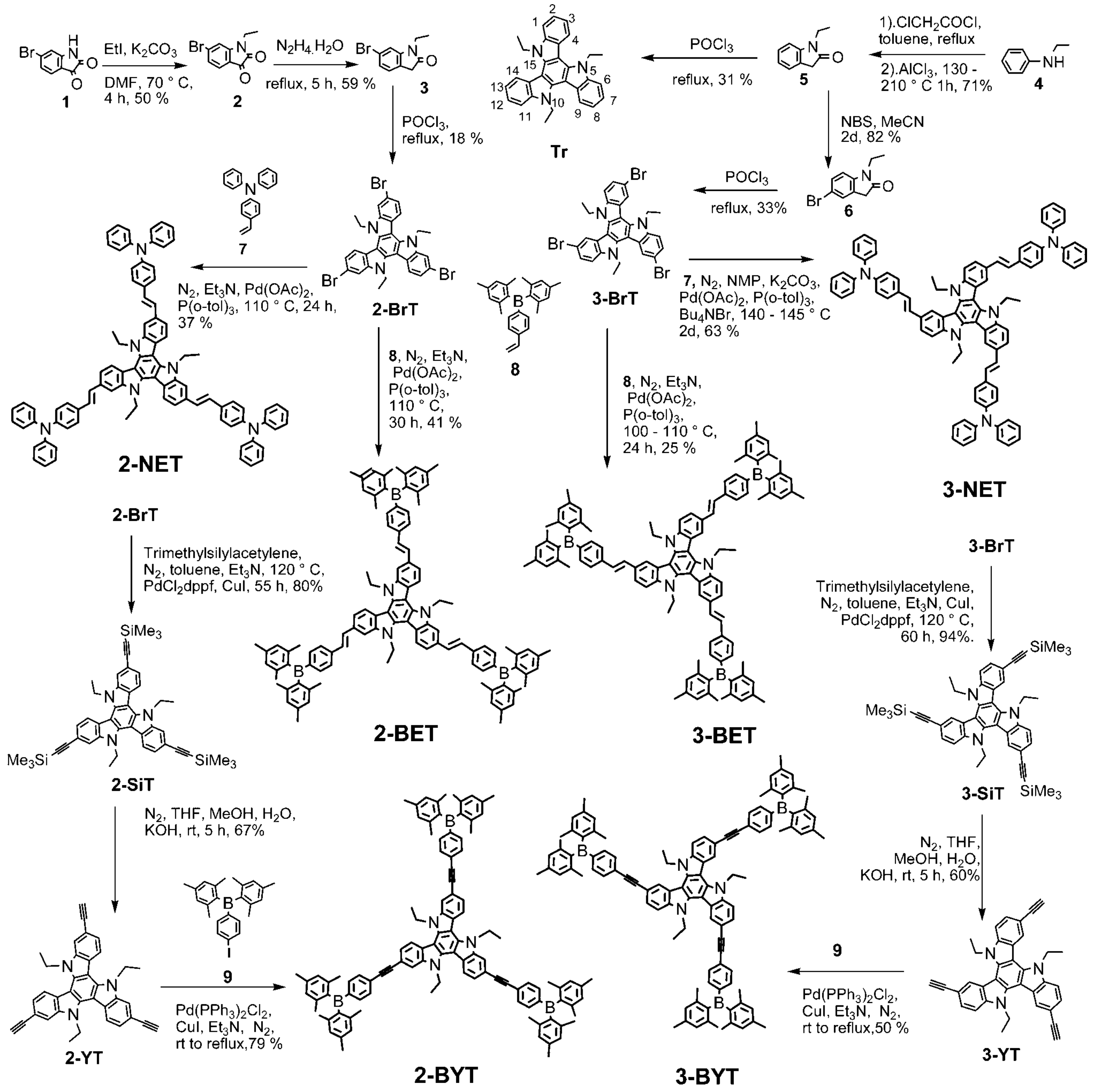
Scheme 1



with aromaticity and electron-donating potential for ICT. Triindole derivatives have also acquired several applications in discotic liquid crystals,[10] hole transporting materials,[11] and in OLEDs,[12] etc. However, to our knowledge, there are no reports about TPA properties of triindole derivatives.

We noticed that triindole has the 3,8,13- or 2,7,12-substitution variety, which allows different ways of π-extension and ICT. In this letter, we report four new D(π-A)$_3$ kinds of triindole derivatives with a large TPA cross section. By bridging the triindole core and triarylboryl via the ethenylene linker at the 3,8,13- or 2,7,12-position, we obtained **3-BET**

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Table 1. Linear and Nonlinear Optical Properties

	λ_{abs}[a] nm	ε[a] M^{-1} cm^{-1}	λ_{em}[a] nm	$\Delta\tilde{\nu}$[b] 10^3cm^{-1}	Φ[c]	δ/GM (λ/nm)[d]	$\Phi\delta$/GM
Tr	316	8.0×10^4	397	6.5	0.17	nondetectable	–
8	323	3.0×10^4	396	5.7	0.15	nondetectable	–
3-SiT	335	6.8×10^4	410	5.5	0.14	nondetectable	–
2-SiT	344	1.4×10^5	428	5.7	0.19	2.1×10^1 (720)	0.40
3-NET	383	1.2×10^5	429	2.8	0.55	3.6×10^1 (810)	2.0×10^1
2-NET	402	1.8×10^5	456	2.9	0.42	4.0×10^2 (810)	1.7×10^2
3-BYT	396	1.2×10^5	506	5.5	0.43	8.7×10^2 (810)	3.7×10^2
2-BYT	399	1.0×10^5	516	5.7	0.60	1.9×10^3 (810)	1.1×10^3
3-BET	412	1.1×10^5	516	4.9	0.33	2.1×10^3 (810)	6.9×10^2
2-BET	427	1.1×10^5	543	5.0	0.40	2.5×10^3 (820)	1.0×10^3

[a] Linear optical properties in 2 μM THF. [b] Stokes shift. [c] Quantum yield. [d] TPA cross section (100 μM in THF), coumarin 307 (100 μM in MeOH) as standard,[15] 1 GM = 10^{-50} cm^4 s $molecule^{-1}$ $photon^{-1}$.

and **2-BET**. The **3-BYT** and **2-BYT** are the results of replacing ethenylene by an ethynylene group. The terminal dimesitylboryl−B(Mes)$_2$ group acts as the electron acceptor and fluorophore.[13] The donor end-capped D(π-D)$_3$ type of compounds, namely, **3-NET** and **2-NET**, are also synthesized for comparison study.

As shown in Scheme 1, **2-BrT** and **3-BrT** precursors were synthesized by trimerization of **3** and **6** in POCl$_3$, respectively.[14] Direct bromination of **5** will provide **6**, rather than **3**, as confirmed by the X-ray structure of **6** (see Supporting Information (SI)). Compound **3** was prepared by reduction of **2**.

2-BET (or **3-BET**) was synthesized through Heck coupling of **2-BrT** (or **3-BrT**) with **8** in the presence of Et$_3$N, Pd(OAc)$_2$, and P(*o*-tol)$_3$ at 110 °C under N$_2$. This concurred with the reports that the −B(Mes)$_2$ group is stable in palladium-catalyzed conditions.[13b,e]

Sonogashira coupling of **2-BrT** (or **3-BrT**) and trimethylsilylacetylene goes smoothly with high yield when catalyzed by PdCl$_2$(dppf), whereas Pd(PPh$_3$)$_2$Cl$_2$ resulted in much lower yield in a similar reaction.[14] The resultant **2-SiT** and **3-SiT** were deprotected yielding **2-YT** and **3-YT**, which were then coupled with **9** to produce **2-BYT** and **3-BYT**, respectively.

The 3,8,13- or 2,7,12-substitution has been confirmed by a satisfactory X-ray structure determination of **6**, **3-SiT**, and **2-SiT** (see SI) and can also be conveniently identified by ^{1}H NMR of the proton on C4. As shown in Figure 1, at the lowest field side of the spectra, the ^{1}H NMR signal of the ^{1}H−C4 of the 3,8,13-substituted triindole derivatives is invariably singlet, while that of the 2,7,12-substituted counterpart is always doublet at relatively higher field.

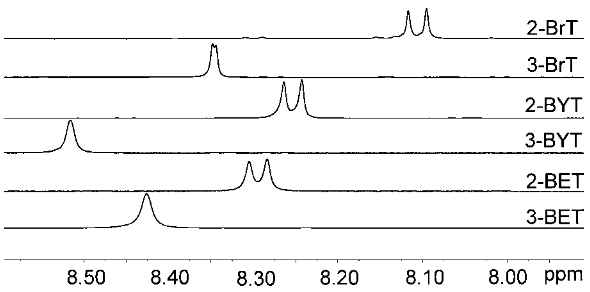

Figure 1. Low-field region of ^{1}H NMR spectra of some 3,8,13- and 2,7,12-substituted compounds in CDCl$_3$.

All the target compounds show high photostability and exhibit strong one-photon absorption (see Table 1), which can be thought of as a prerequisite for large TPA. The **Tr** and **8** building blocks show almost the same peak wavelength, in both the absorption and emission spectra. When joining them up, the spectra of the resultant compounds are greatly red-shifted.

The peak wavelength of the absorption and fluorescence spectra and the Stokes shifts of all the 2,7,12-substituted

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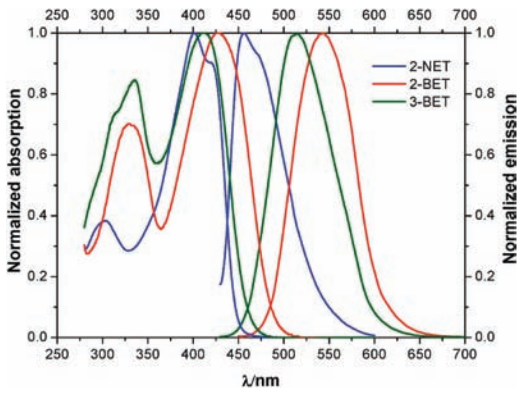

Figure 2. Normalized absorption and emission spectra of **2-NET**, **2-BET**, and **3-BET** in THF.

triindole derivatives are larger than those of their 3,8,13-isomers. The bathochromic of the 2,7,12-compounds indicates that the 2-substitution, in comparison to the 3-substitution, will cause a more effective ICT and a better conjugation. Indeed, the average C−C bond length between the central and outer benzene, measured by X-ray diffraction, is 1.441(3) for **2-SiT** and 1.457(3) Å for **3-SiT** (see SI), demonstrating the better conjugation of the 2,7,12-isomers.

The $-B(Mes)_2$-capped compounds show great bathochromic spectral shift to their $-N(Ph)_2$-capped counterparts. The solvatochromic property of **2-BET** and **3-BET** of the fluorescence spectra is also much larger than that of **2-NET** and **3-NET** (see SI). It is not unexpected that the photon-induced ICT of the $D(\pi\text{-}A)_3$ type octupoles is more pronounced than that of the $D(\pi\text{-}D)_3$ type. Both the absorption and emission of **2-BET** (or **3-BET**) with the ethenylene linker are red-shifted relative to those of **2-BYT** (or **3-BYT**) with the ethynylene linker.

Excited by the femtosecond pulses of a Ti:sapphire laser, the molecular TPA cross section, δ, was determined by using the two-photon excited fluorescence (TPEF) method (see SI for details).[15] As shown in Figure 3 and Table 1, the low-lying TPA peak wavelength of our target compounds are basically twice that of the low-lying one-photon absorption, implying that the one-photon excited state may be identical with the two-photon excied state.

3-SiT has no detectable TPEF signals, while **2-SiT** shows a sizable TPEF intensity. The δ values of the 2,7,12-substituted triindole derivatives are overwhelmingly larger than that of their 3,8,13-isomers in almost all the experimental spectral ranges. The $\Phi\delta$ values (known as TPE action cross section to characterize the TPEF intensity) of all the 2,7,12-isomers are also invariably larger than that of their 3,8,13-counterparts. The excellent TPA property of the 2,7,12-isomers can be attributed to their better conjugation of the triindole core and the strong electronic coupling between the three branches. The 3,8,13-substituted octupoles may be regarded as three weakly coupled N→B dipoles. However, the 2,7,12-octupoles can not be treated by this kind of exciton approach,[8] due to their more extended and complicated way of ICT.

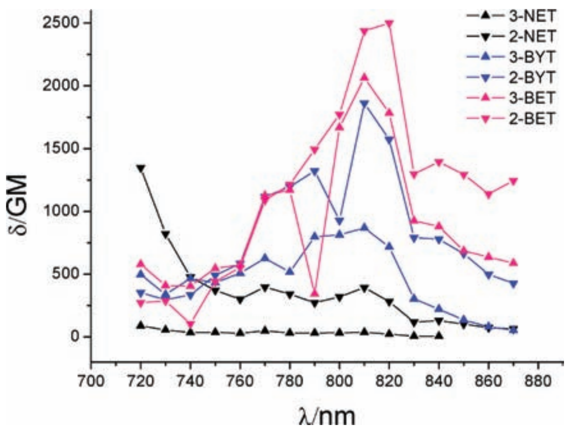

Figure 3. TPA spectra of the title triindole derivatives in THF.

The $-B(Mes)_2$-capped compounds have much larger δ and $\Phi\delta$ values than their $-N(Ph)_2$-capped counterparts in the wide spectral region. It seems certain that the structural factors which bathochromically shift the one-photon spectra will simultaneously enhance the two-photon response of these molecules. The δ value of **2-BET** (**3-BET**) is larger than that of **2-BYT** (**3-BYT**), though **2-BYT** shows the highest $\Phi\delta$ value because of its highest quantum yield Φ. Other compounds with the ethenylene double-bond π-linker were also reported to be more TPA active than their ethynylene triple-bond analogues, and this was attributed to the more efficient ICT of the formers.[3f,16]

In summary, this work revealed the 3,8,13- or 2,7,12-substitution varieties within the octupolar framework of the triindole derivatives. This "position" variable provides extra space, in addition to the π-extension and the donor-or-acceptor functionalization strategies, to fine-tune and optimize molecular structures for TPA. The TPA cross sections of the 2,7,12-substituted compounds (**2-BET**, **2-BYT**, and **2-NET**) are significantly larger than their 3,8,13-isomers (**3-BET**, **3-BYT**, and **3-NET**). We also demonstrated that (1) the ethenylene π-linker is better than the ethynylene linker, and (2) the $D(\pi\text{-}A)_3$ structure is superior to the $D(\pi\text{-}D)_3$, for large TPA. The title compounds or their derivatives may find some applications as optical limiting or fluorescence imaging materials based on their large TPA cross section (δ) and TPE action cross section ($\Phi\delta$).

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Supporting Information Available: Synthetic procedures and characterization data, TEPF graphics, absorption and emission spectra, and X-ray structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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