

Highly Fluorescent Naphthalimide Derivatives for Two-photon Absorption Materials

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Novel multi-branched naphthalimide derivatives (TPA-NA1, TPA-NA2, and TPA-NA3) were synthesized by the Sonogashira reaction of *N*-butyl-4-bromo-1,8-naphthalimide with mono-, di-, and tri-ethynylated triphenylamine. The fluorescence increases with the increase of branch number and the quantum yield is as high as 0.87 for TPA-NA3 in toluene. Two-photon absorption cross sections of TPA-NA1, TPA-NA2, and TPA-NA3 were determined to be $0.42 \times 10^{-20} \text{ cm}^4/\text{GW}$, $1.4 \times 10^{-20} \text{ cm}^4/\text{GW}$ and $1.0 \times 10^{-20} \text{ cm}^4/\text{GW}$ (open aperture Z-scan, 120 fs, 780 nm), respectively.

Great efforts have been devoted to the synthesis of novel compounds with large two-photon absorption (2PA) cross section.^{1–13} 1,8-Naphthalimide compounds are an attractive class of materials for their excellent photophysical and photochemical characteristics. They have been widely used as biological, biomedical, optical, and electronic materials.^{14–17} Until now, no naphthalimide derivatives have been reported as 2PA materials. 1,8-Naphthalimide have high electron affinities and the introduction of electron donating group at the 4-position of 1,8-naphthalimide would increase the fluorescence quantum yield and shifted the absorption and fluorescence maxima to the longer wavelength.¹⁸

In this letter, we use naphthalimide as strong electron acceptor, triphenylamine as electron donor, and acetylene as π -conjugated bridge to form novel one-, two-, and tri-branched compounds (shown in Figure 1). Every branch forms a D- π -A structure and the conjugate system of the molecules is efficiently extended. In TPA-NA3, three D- π -A units forms tri-branched molecular structure.

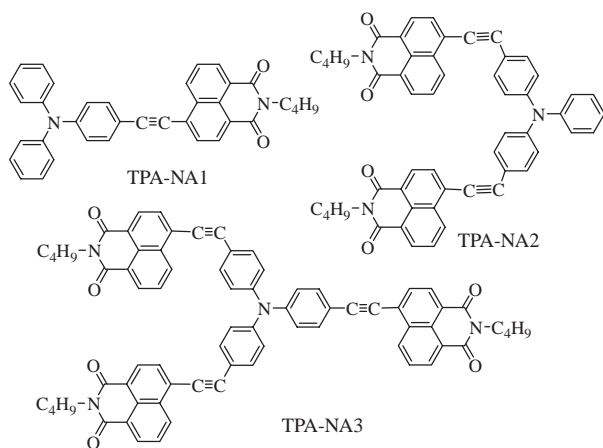


Figure 1. The chemical structures of TPA-NA1, TPA-NA2, and TPA-NA3.

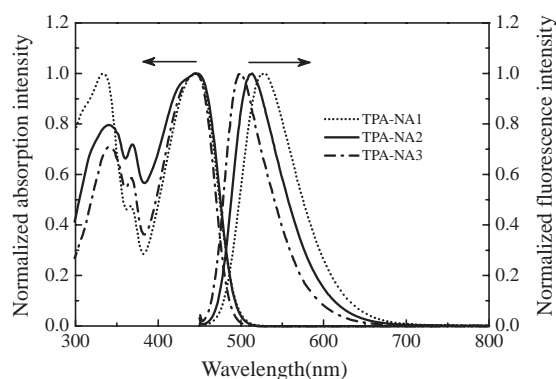


Figure 2. Normalized absorption and fluorescence spectra of TPA-NA1, TPA-NA2, and TPA-NA3 in toluene solution.

Naphthalimide derivatives were synthesized by the Sonogashira coupling reaction of *N*-butyl-4-bromo-1,8-naphthalimide and mono-, di-, and tri-ethynylated triphenylamine with the molar ratio of 1:1, 2:1, and 3:1. The reactions were carried out in triethylamine and tetrahydrofuran (THF) solution for 6 h under the catalyst of $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}$. The final products were purified by chromatography (silica gel) in yield of 40–53.4% and the structures were characterized by $^1\text{H NMR}$ and $^{13}\text{C NMR}$.¹⁹

The linear optical properties of naphthalimide derivatives TPA-NA1, TPA-NA2, and TPA-NA3 were studied in dichloromethane (DCM) and toluene solutions and the data are listed in Table 1. As shown in Figure 2, the compounds exhibit an intense absorption band at about 445 nm, assigning to the π - π^* electron transition, with absorption coefficients in the order of $10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$. The absorption peaks of shorter wavelength at about 340 and 370 nm may arise from the localized electronic transition of the triphenylamine unit and the naphthalimide unit. When changing the solvent from toluene to dichloromethane, the absorption spectra of these compounds change a little and every absorption peaks vary only several nanometers.

In toluene, these compounds emit strong fluorescence with the quantum yields increasing in the order of one-, two-, and three-branched derivatives TPA-NA1, TPA-NA2, and TPA-NA3. This is presumably due to the increased steric hindrance in the branched molecule and the rotation of C–N bonds of triphenylamine is restricted, therefore the nonradiative deactivation of excited state is efficiently prohibited, which leads to the quantum yield as high as 0.87. A rigid molecular structure also confines the excited state nuclear movement and reduces the configuration difference between the excited state and ground state, leading to Stokes shift decreasing with the increase of branch number.

In dichloromethane solution, a similar trend was also observed for these compounds. But in dichloromethane solution,

Table 1. The optical properties of TPA-NA1, TPA-NA2, and TPA-NA3

Compounds	$\lambda_{\max}^{\text{abs}}$ (nm)		ϵ^{a} ($10^5 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$)	$\lambda_{\max}^{\text{fl}}$ (nm)		Stokes shift (nm)		Φ^{b}		σ^{c}	
	Toluene	DCM		Toluene	DCM	Toluene	DCM	Toluene	DCM	$10^{-20} \text{ cm}^4/\text{GW}$	GM
TPA-NA1	445	448	0.50	530	639	85	191	0.69	0.061	0.42	107
TPA-NA2	446	452	0.91	516	632	70	180	0.82	0.077	1.4	360
TPA-NA3	448	454	1.42	502	617	54	163	0.87	0.15	1.0	250

^aMolar absorption coefficients in toluene solution. ^bFluorescence quantum yield determined using *N*-butyl-4-amino-1,8-naphthalimide ($\Phi = 0.64$) as the standard.²⁰ ^c2PA cross sections in toluene measured at 780 nm (120 fs).

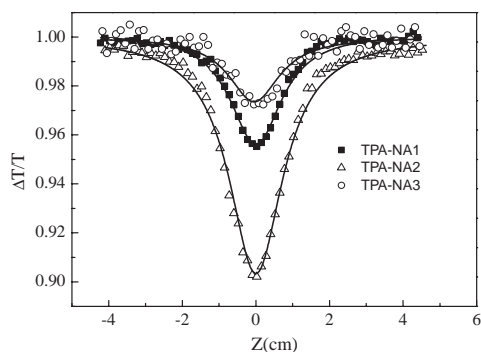


Figure 3. The experimental (scattered symbols) and fitting (solid line) results of open-aperture Z-scan experiments.

the fluorescence quantum yield is nearly one order magnitude lower and the Stokes shift is larger than 100 nm compared with those measured in toluene solution. The solvent effect on fluorescence spectra is more pronounced than that on absorption spectra, which means the dipole moment in the excited state is much larger than that in the ground state.

2PA cross sections of these compounds in toluene solution were determined by the open aperture Z-scan technique with 120 fs, 780 nm laser pulses.¹⁹ The experimental data and theoretically fitted results are shown in Figure 3. The 2PA cross section of TPA-NA1, TPA-NA2, and TPA-NA3 were measured to be $0.42 \times 10^{-20} \text{ cm}^4/\text{GW}$, $1.4 \times 10^{-20} \text{ cm}^4/\text{GW}$, and $1.0 \times 10^{-20} \text{ cm}^4/\text{GW}$, respectively. These values are comparable to most of representative materials with similar molecular weight.^{8–11} The high 2PA properties of these molecules are attributed to the extended π -system and enhanced intramolecular charge transfer from triphenylamine to naphthalimide. The proportionality between 2PA coefficient and the incident power shows that 2PA is a dominating process and excited states absorption can be neglected.¹⁹

Owing to the multi-branched structure, the 2PA cross sections of TPA-NA2 and TPA-NA3 are much larger than that of TPA-NA1. But the value of TPA-NA3 is even smaller than that of TPA-NA2, which seems to be contrary to the general conclusion that the 2PA cross section of multi-branched compound is increased with chromophore density. This phenomenon is hard to explain now and may be related to the 2PA cross section dependence with the wavelength. We can not measure the 2PA cross section profile at different wavelength at present because of the limit of our laser apparatus. More experiments need to be conducted to see if the 2PA cross section of TPA-NA3 is larger than TPA-NA2 at other wavelengths.

In summary, multi-branched naphthalimide derivatives with high fluorescence have been synthesized and their linear and two-photon photophysical properties were studied. The high

sensitivity of fluorescence on solvent polarity makes these compounds possible to be used as potential 2PA polarity probes.

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- The detailed synthesis of the compounds and the measurement of 2PA cross sections are shown in the Electronic Supporting Information.
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