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New Fluorophores Based on Trifluorenylamine with Very Large Intrinsic Three-Photon Absorption Cross Sections

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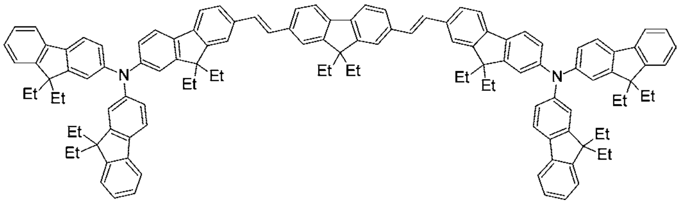
ABSTRACT



A new fluorophore, tri(9,9-diethyl-9*H*-fluorenyl)amine, was synthesized by the Buchwald–Hartwig reaction of 2-aminofluorene, and based on this molecule three more fluorophores were prepared that exhibit a very large intrinsic three-photon absorption in the near-IR region, which scales as a third power of the bridge length.

Multiphoton absorption, mainly two-photon (2PA) and three-photon (3PA) absorption, has attracted considerable interest since the mid-1990s due to its potential applications ranging from high capacity data storage and[1,2] biological imaging [3,4] to photodynamic therapy[5,6] and 3D nano-/microfabrication.[1,7] Many different types of compounds have been investigated for their multiphoton absorption, and it has been found that the intramolecular charge-transfer efficiency[8,9] and the size of the effective conjugation domain[10−13] play crucial roles in increasing the 2PA cross section. However, the study of how to increase the 3PA cross section of organic compounds is still very limited.[12−25] Recently, we reported on 2PA and

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3PA of three-arm and four-arm dendrimers based on 4,4′-bis(diphenylamino)stilbene (BDPAS) and 4,4′-bis-(diphenylamino)distyrylbenzene (BDPADSB) repeat units and found that the cooperative enhancement of 2PA and 3PA is directly related to the size of the effective conjugation domain.[10−13] We also showed [10−13] that in the higher dendrimer generations the effective conjugation is limited within the segments of the molecule, partially due to the torsion of the branches. Since the dendrimers based on triphenylamine units demonstrated a record large increase of the nonlinear cross sections,[10−13] we are interested in whether replacing the phenyl rings in triphenylamine with an even larger yet flat aromatic system, such as fluorenyl rings, might further advance this unique property.

In the few previous reports on nonlinear-optical compounds comprising fluorenyl units, the fluorenyl was used only as a π bridge[23,26−29] rather than as the principal building unit. Shirota's group reported a molecule with di(9,9-dimethyl-9*H*-fluorenyl)amino moiety,[30] but its multiphoton absorption was not studied. Furthermore, only very few reports on the Buchwald−Hartwig reaction of 2-aminofluoene with other aromatic halogens have been presented so far.[31,32] In this paper we present the synthesis of a new series of fluorophores based on the tri(9,9-diethyl-9*H*-fluorenyl)amine unit and study their linear and nonlinear absorption properties.

The reaction between 2-aminofluorene (**1**) and 2-bromo-9,9-diethyl-*9H*-fluorene (**2**) with $Pb_2(dba)_3$ and 1,1′-ferrocenebis(diphenylphosphine) (DPPF) as catalysts in toluene afforded yellow crystals of **3** with the yield of 78.4% after chromatographic purification followed by recrystallization, whereas an attempt to substitute the amino hydrogen of **3** with excess **2** in a one-pot reaction did not give the target compound, **5**. The third fluorenyl group was introduced by reacting 1.05 equiv of 9,9-diethyl-2-iodo-9*H*-fluorene(**4**) with **3** in the dark with the catalysts $Pb(OAc)_2$ and $P(^tBu)_3$ to give **5** in a yield of 80.9%. A lower yield of **5** was obtained if this reaction was run in a continuous two-step way with $Pb_2(dba)_3$, DPPF as catalysts without the separation of **3**. The methylene protons in **5** could be replaced easily with bromoethane in DMSO or DMF at 40−50 °C to afford a symmetrical molecule, tri(9,9-diethyl-9*H*-fluorenyl)amine (TFA), with the yield of 90.9%. TFA could be easily brominated with bromine or NBS at the 7-position to give monobromide and tribromide, similar to its phenyl analogue, triphenylamine. However, the preparation of the monoaldehyde of TFA, 7-bis(9,9-diethyl-9*H*-fluorenyl)amino-9,9-diethyl-9*H*-fluorene-2-carboxaldehyde (**9**), was not successful either by direct formylation (Vilsmeier−Haack reaction) or bromination followed by the reaction with butyllithium and anhydrous DMF. The reason for this failure is not very clear and the relatively low reactivity of the hydrogene/bromine atom at 7-position of fluorenyl ring is suspect.

Compound **9** was prepared with an overall yield of 56.4% by first reacting 7-bromo-9,9-diethyl-9*H*-fluorene-2-carboxaldehyde (**6**) with **1** and then with **4** followed by replacing the methylene protons with bromoethane. The fluorophore TFA01 was prepared by the reaction between 9,9-diethyl-2,7-diiodo-9*H*-fluorene (**11**) and **3** with $Pb(OAc)_2$ and $P(^tBu)_3$ in toluene. TFA02 and TFA03 were prepared from **9** by the reaction with $TiCl_4$/Zn or **10** in THF, respectively.

The solubility of TFA01, TFA02 and TFA03 in CH_2Cl_2, $CHCl_3$, and toluene increases as more 9,9-diethylfluorenyl units are introduced into the molecule. This is somewhat surprising because in an oligomer series the solubility usually decreases when the size of the molecule increases, cf. BDPAS and BDPADSB. Actually an attempt to replace the methylene protons in TFA01 with ethyl groups gave some very insoluble solids that were difficult to purify by chromatography.

All TFA01, TFA02, and TFA03 molecules show two major absorption bands (in TFA01 only a shoulder is observed in place of long wavelength band), one of which (short wavelength) is at ca. 380 nm and remains almost unchanged for all three fluorophores, while the other one (long wavelength) shows a large shift from ca. 405 nm (TFA01, shoulder) to 427 nm (TFA03). Our study of fluorescence anisotropy as a function of exciation wavelength in viscous liquid demonstrates that the angle between the short- and long-wavelength transition dipoles is 57° in TFA01 and 52° in both TFA02 and TFA03. These data imply that the higher-energy transition is most probably polarized along the outer N−C bonds of the ending trifluorene moieties, whereas the lowest transition is polarized along the π-conjugated bridge system and the conjugation length increases with the number of fluorenes in the bridge. In the following discussion we will therefore concentrate on 3PA properties of the longer-wavelength transition.

As for fluorescence properties,the emission maxima of TFA02 and TFA03 shift, as compared to TFA01, to longer wavelengths by ca. 80 and 90 nm, respectively, which can

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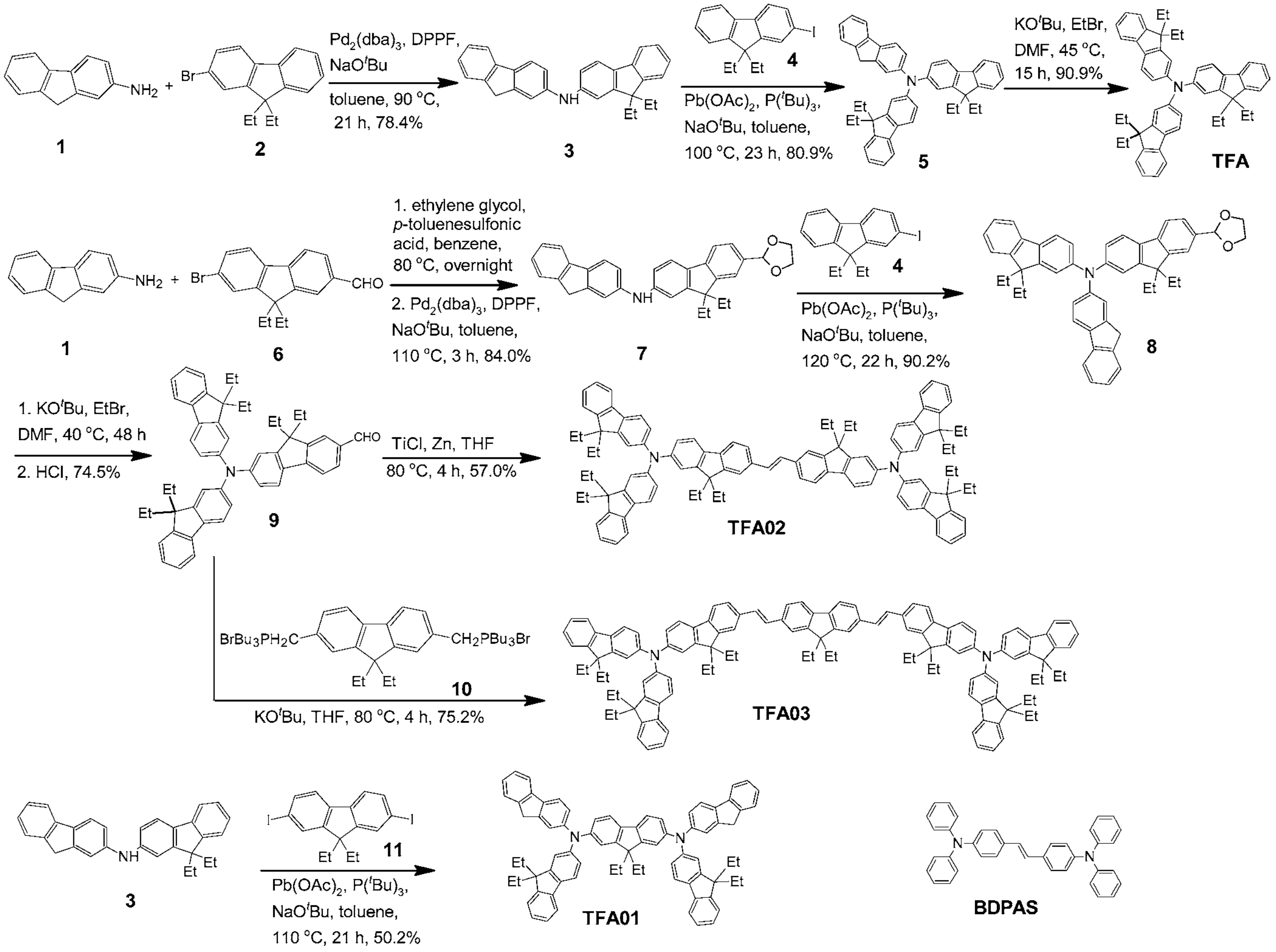
Scheme 1. Synthesis of Fluorophores of the TFA Family



be explained by a longer π-conjugation system and, probably, by more profound structural reorganization in larger molecules in the relaxed excited state (because the Stokes' shift also increases). Also, the building block of our series, the TFA molecule, possesses much stronger fluorescence and longer wavelength absorption and fluorescence maxima compared to the triphenylamine molecule, which can imply stronger conjugation over the lone electron pair of the nitrogen atom in the former.[33,34] The fluorescence quantum yield of TFA the and TFA01−TFA03 series is close to 0.4 and slightly decreases with the increase of molecular size. This can be connected with faster nonradiative relaxation in larger molecules, because of the lower energy of the emitting state in them.

Three-photon absorption measurements were performed by exciting the sample with femtosecond laser pulses and recording its fluorescence spectrum. The 3PA cross sections, σ_3, were measured by comparing the intensity of fluorescence of the investigated compound with that of BDPAS. For this latter molecule the absolute 3PA absorption spectrum was measured [12,13] and its maximum cross section is reproduced quite well by quantum-mechanical calculations,[35] which makes it a good benchmark compound for 3PA measurements in the spectral region from 1140 to 1320 nm. 3PA spectra were measured by tuning the laser wavelength and recording the fluorescence intensity at constant excitation photon flux and pulse duration. Our experimental setup for 3PA measurements was reported before.[12,13] Briefly, we used for excitation an optical parametric amplifier (TOPAS, Quantronix) that generates 100-fs pulses in the wavelength range from 1100 to 1600 nm at a 1-KHz repetition rate. The samples were prepared as dichloromethane solutions at the concentration of $\sim 10^{-4}$ M for 3PA measurements.

The 3PA data are shown in Table 1, and the full 3PA spectrum of TFA03 is shown in Figure 1 as an example. Similarly to TFA03, other molecules of the series show 3PA spectra generally following the corresponding 1PA spectra. We present in Table 1 the maximum values of the 3PA cross section, $\sigma_{3,\max}$, in the long-wavelength transition. First of all,

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Table 1. Linear Absorption and 3PA Data of TFA, TFA01, TFA02, and TFA03 in Dichloromethane[a]

molecule	λ_{max} (nm)	ϵ ($M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)	Φ_f[b]	λ_{3PA} (nm)	$\sigma_{3,max}$ (10^{-80} cm^6 s^2)
TFA	373	5.9×10^4	416	0.47	1190	0.21[c]
TFA01	375	9.5×10^4	428	0.43	1218	1.1[c]
	406 (sh)	6.2×10^4				
TFA02	380	10.7×10^4	512	0.41	1269	5.3[c]
	423	10.5×10^4				
TFA03	381	1.54×10^5	520	0.38	1284	18[c]
	427	1.95×10^5				

[a] λ_{max}: linear absorption maximum. ϵ: extinction coefficient at λ_{max}. λ_{em}: fluorescent emission maximum. Φ_f: fluorescent quantum yield. λ_{3PA}: spectral maximum of the longest-wavelength 3PA transition. $\sigma_{3,max}$: 3PA cross-section at λ_{3PA}. [b] Measured with respect to 9-methyl-anthracene in benzene, for which $\Phi_f = 0.49$.[36] [c] The error range is ±25%.

whereas linear extinction coefficient scales almost linearly with the length of the bridge, the integrated 3PA strength, namely, $\sigma_3\nu_{max}{}^4\Gamma$ where ν_{max} and Γ are the maximum frequency and the width of 3PA transition, scales as 1:8.1:26 for TFA01, TFA02, and TFA03 series. This behavior is very well described by a cubic law of the number of fluorenyl units between two nitrogens (1:2:3, respectively), which suggests the complete π-electronic conjugation[12,13] in the bridge. As for the quantitative values, compared to its triphenylamine analogue (BDPAS),[12,13] TFA02 demonstrates a 10 times larger maximum 3PA cross section. The $\sigma_{3,max} = 1.8 \times 10^{-79}$ cm^6 s^2 value, measured for TFA03 in its spectral maximum at 1284 nm (see Figure 1), is to the best of our knowledge one of the highest intrinsic 3PA cross section, measured so far for any organic molecule.[12,13] We emphasize one more time that we deal here with intrinsic σ_3 values, which were obtained with femtosecond fluorescence technique. Nonlinear transmission methods, especially in combination with pico- and nanosecond excitation, usually overestimate the cross sections by several orders of magnitude due to excited-state absorption, self-focusing, and other nonlinear contributions. For example, 3PA cross section of 2,7-bis(diphenylamino)-9,9-didecyl-9*H*-fluorene in hexane was measured with 35 ps pulses and *z*-scan technique at 1110 nm to be $\sigma_3 = 8.2 \times 10^{-77}$cm^6 s^2.[23] On the other hand, our independent measurement of very similar compound, 2,7-bis(diphenylamino)-9,9-diethyl-9*H*-fluorene, in hexane at 1170 nm with 100-fs laser and fluorescence technique gave $\sigma_3 = 1 \times 10^{-81}$cm^6 s^2. Taking into account that we do not exactly reach the maximum (which is near 1120 nm), we estimate that the picosecond *z*-scan technique exaggerates the intrinsic value by ~4 orders of magnitude.

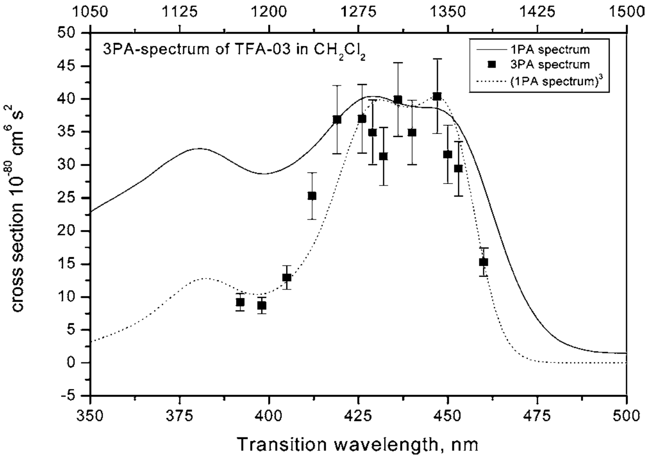

Figure 1. Linear absorption and 3PA spectrum of TFA03 in CH$_2$Cl$_2$

Our data on TFA series of molecules strongly imply that both the replacement of phenyl rings in a conjugation system with larger yet flat aromatic fluorenyl rings and enlargement of the peripheral aromatic groups significantly enhance the 3PA cross section.

In summary, we synthesized the new family of fluorophores based on tri(9,9-diethyl-9*H*-fluorenyl)amine by Buchwald−Hartwig amination. These fluorophores show very large 3PA cross sections that are cooperatively enhanced as a result of the complete π-conjugation of the oligo-fluorenylvinylene bridge.

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Supporting Information Available: Spectroscopic data and synthesis procedures for TFA, TFA01, TFA02, and TFA03. This material is available free of charge via the Internet at http://pubs.acs.org.

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