Toward Highly Active Two-Photon Absorbing Liquids. Synthesis and Characterization of 1,3,5-Triazine-Based Octupolar Molecules

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Three novel two-photon absorbing (TPA) chromophores with 1,3,5-triazine as the π-electron deficient core, dialkylfluorene as aromatic bridges, and diphenylamino groups as the electron-donating end-groups were prepared. Designated as **AF-450** (2,4,6-tris[7-(diphenylamino)-9,9-didecylfluoren-2-yl]-1,3,5-triazine), **AF-455** (2,4,6-tris[9,9-bis(3,7-dimethyloctyl)-7-(diphenylamino)-fluoren-2yl]-1,3,5-triazine), and **AF-457** (2,4,6-tris[(7-(diphenylamino)-9,9-diprop-2-enylfluoren-2-yl]-1,3,5-triazine), their overall molecular structure and local symmetry (D_{3h}) are similar to those of previously reported three-armed **AF-350** (*N*,*N*,*N*-tris[4-{7-(2-benzothiazolyl)-9,9-diethylfluoren-2-yl}phenyl]amine) and **AF-380** (*N*,*N*,*N*,-tris[7-(2-benzothiazolyl)-9,9-diethylfluoren-2-yl]amine). Among the family of AFX chromophores previously reported by us, **AF-450** possesses one of the largest *effective* TPA cross-sections ($\sigma_2' =$ 39 500 $\times$ 10^{-50} cm^4-sec/photon-molecule, or 39 500 GM) as determined by nonlinear transmission method in the nanosecond regime at 800 nm. In contrast, **AF-455**, a mixture of stereoisomers with the same chemical formula as **AF-450**, is a glassy material that becomes fluid (molasses-like) upon heating at 70−80 °C and has noticeably smaller effective σ_2' value (33 300 GM). **AF-457** ($\sigma_2' =$ 27 800 GM) with six allyl side groups was prepared as a precursor toward the synthesis of a TPA liquid. The intrinsic TPA cross-sections of these chromophores were also determined as a function of excitation wavelengths via a femtosecond white-light continuum generation and direct degenerate-TPA measurement technique. At the TPA peaks ~779 nm, their σ_2' values are 216, 214, and 199 GM (±15%) for **AF-450**, **AF-455**, and **AF-457**, in that order. They are in the same trend as the nanosecond values, albeit two orders of magnitude lower.

Introduction

Two-photon absorption (TPA) is a well-known phenomenon in nonlinear optics since Göppert-Mayer's ground-breaking theoretical work in 1931[1] and the experimental verification reported by Kaiser and Garrett in 1961.[2] Its practical importance has been recognized by various pioneering efforts such as two-photon spectroscopic studies of biological molecules (Birge et al.),[3] two-photon upconverted fluorescence microscopy (Webb et al.),[4] and TPA-based photochromic optical data storage (Rentzepis et al.).[5] However, the early development of TPA-based applications was slow chiefly because the available materials had relatively small two-photon cross-sections. Then, in the mid-to-late 1990s, the momentum for the research-and-development activities in this field was accelerated by the discoveries of several classes of organic chromophores with very high two-photon responses.[6,7,8] In the wake of these discoveries, significant advances have been made in the design and synthesis of two-photon absorbing materials

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with very large cross-section (σ_2') values.[9] In the meantime, the isolation of biological macromolecules with very large two-photon absorptivities has also been claimed.[10] Arguably, these new materials have provided a technological push for a broad spectrum of TPA-based application areas in photonics[4,5,11] and biophotonics[12] including microscopy, data storage, microfabrication, laser protection, photodynamic therapy, etc. Although further enhancement of TPA cross-section value is still possible as suggested by a number of theoretical studies,[13] for certain applications the two-photon-property requirement has essentially been met by the state-of-art materials. Furthermore, we feel that the secondary properties, namely physical, thermal, and mechanical properties that are important to material processing and device fabrication, should not be neglected and must be addressed in parallel with the continuing efforts to enhance the effective σ_2' values. Depending on specific applications, TPA materials may be useful as films, fibers, or neat liquids, and the requirements for the secondary properties are expected to be different. The need for such liquids was inspired by the report on a two-photon resonance-enhanced refractive-index change and self-focusing in a dye-solution-filled hollow optical fiber system.[14] Ostensibly, replacing the TPA dye solution with a TPA neat liquid should result in higher number density, and in turn, greater nonlinear optical effect.

This paper describes the progress of our effort in developing highly active TPA liquids at low temperatures (25−75 °C) with respect to the synthesis, thermal, spectroscopic, and nonlinear optical characterization of three new diphenylaminofluorine-1,3,5-triazine-based chromophores.

Results and Discussion

Molecular Design Consideration. Among our AFX chromophores that were previously reported, **AF-350** and **AF-380** are two of the most active two-photon absorbing compounds.[7d,11g,15] They represent a generic structural motif that is two-dimensional (quasi-planar), with the single triarylamino group serving as the electron-rich hub, dialkylfluorenyl bridges, and three π-deficient benzothiazole occupying the termini (Figure 1). The overall molecular structure is ideally symmetrical and of push−pull type with respect to the excited-state charge redistribution. The local molecular symmetry of NC_3 is D_{3h} and molecules with such symmetry belong to an interesting class of nonlinear optical molecules known as octupoles.[16] The alternative to this structural motif will be simply switching the π-electron nature of the hub with that of the terminal functional groups. To explore this alternative concept, we have chosen 1,3,5-triazine as the hub moiety and diphenylamines as the π-electron donating end-groups. 1,3,5-Triazine has two important properties that make it ideal: (i) with its ionization potential value of 11.67 eV, it is more π-electron deficient than pyridine (9.73 eV), pyridazine (10.61 eV), pyrimidine (10.41 eV), and

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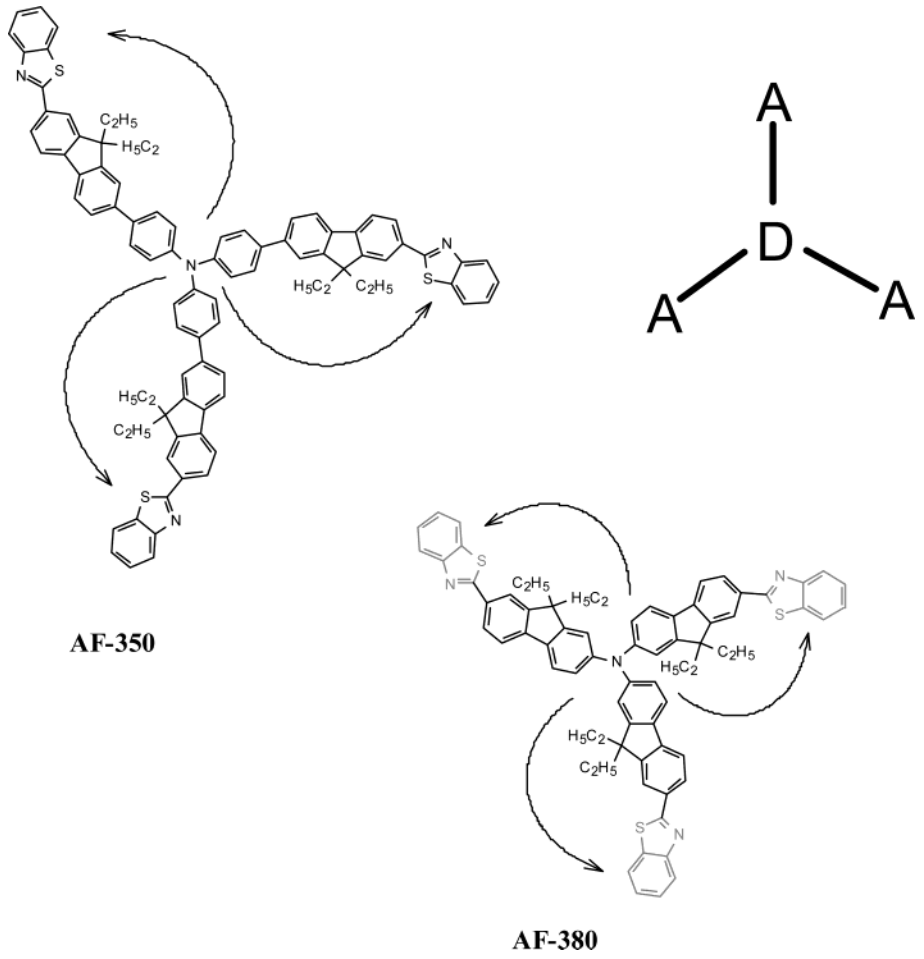

Figure 1. Molecular Structures of **AF-350** and **AF-380**.

pyrazine (10.18 eV);[17] (ii) unlike benzene ring, connecting three aromatic rings at the 2, 4, and 6 positions of 1,3,5-triazine will not create the steric interactions of the ortho-hydrogens. As a result, coplanarity is most probable[18] with the ramification of extended electronic delocalization between 1,3,5-triazine and the aryl rings as well as within the 1,3,5-triazine ring (Figure 2). Molecular modeling of similar 1,3,5-triazine-based octupolar molecules by ab initio and PM3 semiempirical methods and the related electrochemical studies support such a conclusion.[19] A number of octupolar molecules based on a 1,3,5-triazine core and electron-donating substituents have been initially considered for second-order nonlinear optical properties,[20] leading to compounds exhibiting very high hyperpolarizabilities (β).[21]

With respect to engineering the liquidlike characteristics at reasonably low temperatures (e.g., 25−80 °C), there are several approaches that can be used to frustrate or completely preclude the crystallization process of the TPA molecules without a priori compromising their nonlinear optical activities, such as (a) introduction of sufficiently long and highly branched, inert side groups that would not electronically interact (i.e., photoinactive) with the TPA-active unit, (b) same-pot synthesis of isomeric mixtures with different branched alkyl chains, (c) physical blends with TPA molecules with various noncrystallizable side groups, or (d) incorporation of structural features to promote ionic-liquid[22] properties. Approaches (a) and (b) would require the strategic functionalization of the 1,3,5-

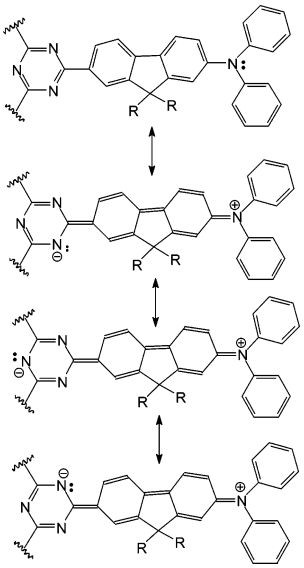

Figure 2. Resonance structures of **AF-450**, **AF-455**, and **AF-457** (only shown for one arm of the molecules).

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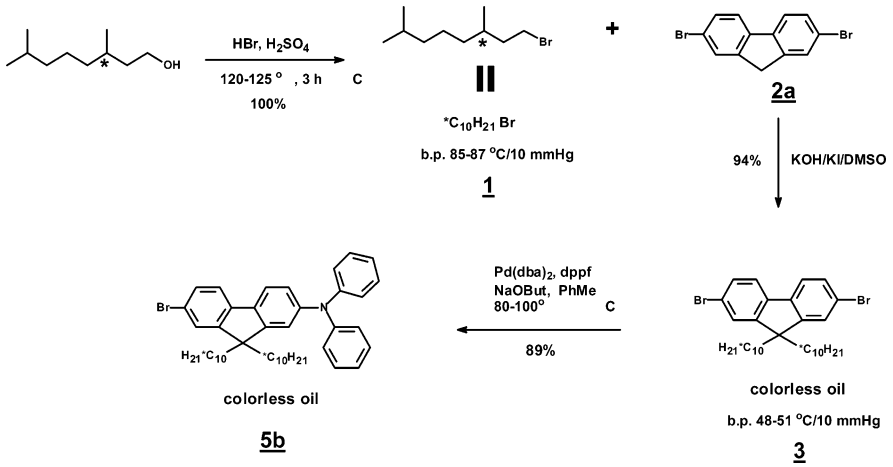

Figure 3. Synthesis of the intermediate, [9,9-bis(3,7-dimethyloctyl)-7-bromo-fluoren-2-yl]diphenylamine (**5b**).

triazine-based octupolar molecules so that the electronic properties of the fluorene bridges and the electron-donating and oxidative stability of the diphenylamino termini would not be adversely affected. In addition, the issues of practicality in synthesis of the designed chromophores, such as the availability and economics of starting materials as well as the synthetic tools for chemical transformation, were factored in our consideration. Thus, we chose to focus first on functionalizing the 9,9-positions of the fluorene bridges even though the phenyl rings of the diphenylamino groups, especially the 3,4,5-positions, are also functionalization possibilities.

As for the molecular structure of **AF-455**, we selected 3,7-dimethyloctyl (trivial name: dihydrocitronellyl) because it is a relatively long branched alkyl chain with an asymmetric (chiral) carbon atom. The combination of these two structural features allows us to apply simultaneously both tactics (a) and (b) outlined in the foregoing paragraph. Furthermore, since there are 6 chiral centers per molecule, the maximal number of stereoisomers or isomer number[23] is $2^6 = 64$, in other words, 32 pairs of enantiomers ("left-hand" and "right-hand" pairs) are possible at the first approximation. After the elimination of duplicates associated with the meso-isomers, the actual isomer number for **AF-455** is determined to be ten. These stereoisomers are 2 meso-isomers and 4 pairs of enantiomers.[24] In addition to being an isomeric blend, nearly half of the mass of **AF-455** is contributed by the branched alkyl side-chains. On the basis of these considerations, we would expect **AF-455** to be amorphous with relatively low glass-transition temperature. We also synthesized **AF-450** which is a structural isomer of **AF-455** with an identical chemical formula ($C_{138}H_{174}N_6$) so that it can serve as a reference point on the crystallization behavior of 1,3,5-triazine with respect to the six linear octyl chains. **AF-457** was prepared because the allyl groups can provide the easy entry to further branching at the 9,9-position, for example via hydrosilation with trialkylsilane.

Synthesis and Thermal Properties. The syntheses of **AF-450**, **AF-455**, and **AF-457** are briefly described in the following paragraphs. The key intermediates to these 1,3,5-triazine-based chromophores have the generic structure of 7-bromo-9,9-dialkylfluoren-2-yl)diphenylamine (with variable alkyl groups). We have reported the preparation of 7-bromo-9,9-didecylfluoren-2-yl)-diphenylamine (**5a**) in a previous paper.[7b] The yield of **5a** could be improved in the Pd-catalyzed amination step by using 1,1′-bis(diphenylphosphino)ferrocene (DPPF; 69% yield) instead of tri-*o*-tolylphosphine (35% yield) and an excess amount of the dibromofluorene precursor. However, we also find that **5a** could be obtained by a copper-catalyzed amination of 2-iodo-7-bromo-9,9-didecylfluorene, under conditions similar to those employed for the arylation of amides.[25] In this case, the high conversion to the product and the complete consumption of the starting dihalofluorene in the Ullmann amination reaction have made the isolation of the desired product easier during the workup.

Similarly, the synthesis of [9,9-bis(3,7-dimethyloctyl)-7-bromo-fluoren-2-yl]diphenylamine (**5b**) and 7-bromo-9,9-diallylfluoren-2-yl)diphenylamine (**5c**) were conducted via synthetic schemes depicted in Figure 3 and Figure 4, starting from 2,7-dibromofluorene or 2-bromo-7-iodofluorene. Whereas 1-bromodecane and allyl bromide are available commercially, the racemic 3,7-dimethyloctyl bromide (required for the preparation of **5b**), was easily obtained from the conversion of the corresponding alcohol with HBr/H_2SO_4 reagents (Figure 3). Also, the palladium-catalyzed mono-amination[26] of the dibromofluorene intermediate **3** leading to **5b** was rather straightforward.

In contrast, we note that **5c**, when generated from a precursor, 2,7-dibromo-9,9-diallylfluorene, under the palladium catalysis was contaminated with an allyl-rearrangement product. In addition, under most amination conditions, using copper and copper salts, we observed that another precursor, 7-bromo-2-iodo-9,9-diallylfluorene (**4**) on reaction with diphenylamine

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(24) This is arrived at in the following way: each fluorene containing two alkyl groups consists of 3 compounds, one meso (RS), and a pair of enantiomers, (R,R) and (S,S). These 3 compounds are individually denoted as A, B, and C. The total combinations of the three letters, where the same 3 letters are not repeated in any one combination will be 10. The combinations AAA and ABC are the two meso-iomers. The other 8 are 4 pairs of enantiomers.

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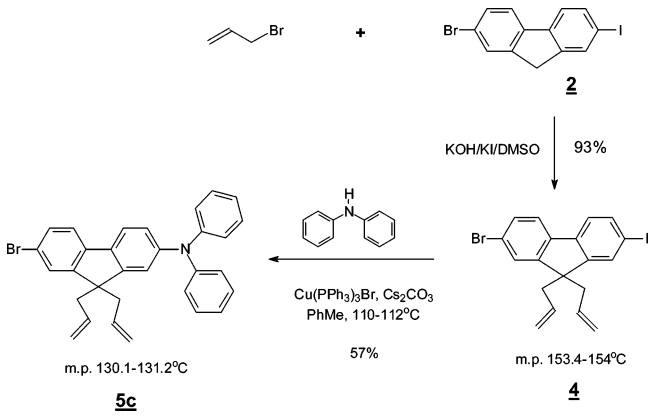

Figure 4. Synthesis of the intermediate 7-bromo-9,9-diallylfluoren-2-yl)diphenylamine (**5c**).

generated a 3:1 product mixture of 7-bromo- and (7-iodo-9,9-diallylfluoren-2yl)diphenylamines. Notwithstandingly, we were able to achieve the exclusive formation of **5c** when the Ullmann amination reaction was conducted with copper bromide complexed with triphenylphosphine and at a lower reaction temperature.[27]

Finally, a lithiation of the respective 7-bromo-9,9-dialkylfluoren-2-yl)diphenylamine with *n*-butyllithium in THF at −78 °C, followed by the addition of one-third equivalent of 1,3,5-trifluoro-1,3,5-triazine (cyanuric fluoride) resulted in the isolation of the respective chromophores, **AF-450** (**6a**, R = *n*-decyl), **AF-455** (**6b**, R = 3,7-dimethyloctyl), and **AF-557** (**6c**, R = allyl); see Figure 5.

As we expected, both the decyl-containing **AF-450** (mp 121−122 °C) and allyl-containing **AF-457** (mp 235−237 °C) were obtained as crystalline compounds, whereas **AF-455** was initially a yellow, iridescent, slow-flowing, viscous oil after the solvent (methylene chloride) had been removed via a rotary evaporator. However, upon standing at room temperature for several weeks, **AF-455** became a glassy solid, probably due to the slow evaporation of the residual methylene chloride. Alternatively, immersion of the viscous oil in 2-propanol in a refrigerator can speed up the solidification process. This glassy solid, however, can be induced to be fluidlike by heating it on a hot-plate to about 70−80 °C. When a small sample was quickly pulled from the viscous melt with a pointed spatula, a relatively long and glasslike fiber could be obtained. A preliminary observation[28] indicated that such fiber showed wave-guiding properties. When a sample of glassy **AF-455** was subjected to a differential scanning calorimetric (DSC) run, it exhibited a small, sharp melting endothermic at 63 °C (∼6 J/g vs 70−100 J/g observed for other crystalline AFX chromophores prepared in our laboratory), and a glass transition at 54 °C upon rescanning after previously heating to 400 °C (see Figure 6). No recrystallization was detected upon cooling, implying that **AF-455** is basically a low-order material. The thermogravimetric analysis (TGA) of **AF-455** indicates that it is relatively robust, and no degradation has been observed below 355 °C in air and 428 °C in helium. The percentages in the weight losses for the first major decomposition in both atmospheres (∼32% in helium and 40% in air) roughly correspond to the weight percent of the alkyl groups (44%) that are the thermally weakest parts of the molecule.

Linear and Nonlinear Optical Properties. The linear optical and two-photon properties for the newly synthesized dyes are summarized in Table 1. The effective TPA cross-sections (±15% uncertainty) were measured by a nonlinear transmission (NLT) technique[7b,29,30] in THF solution[31] at 800 nm with 8-ns laser pulses. This table includes values for β, the two-photon absorption coefficient, σ_2', the two-photon absorption cross-section,

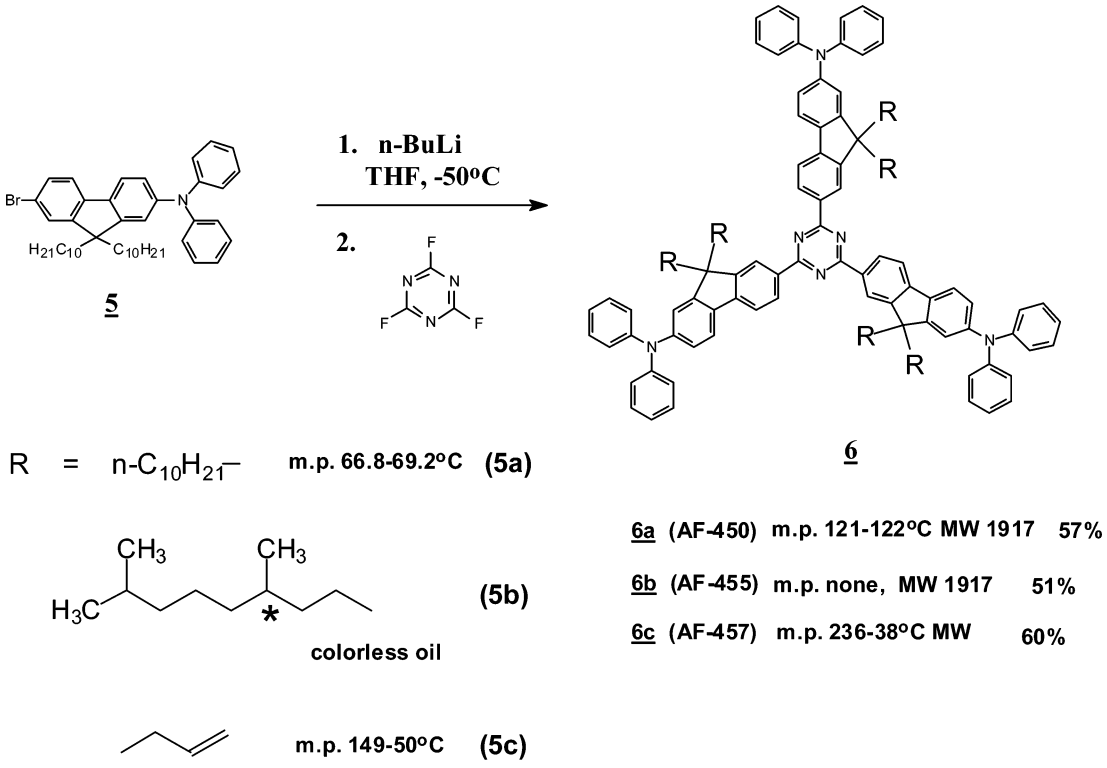

Figure 5. Syntheses of **AF-450**, **AF-455**, and **AF-457**.

Table 1. Physical and Optical Data for AF-450, AF-455, and AF-457

chromophore (MW)	mp (°C)	wt. % alkyl groups	λ_{max} (nm)[a] linear abs. [emission, excited at 410 nm; Φ_f]	β[b] cm/GW at 0.2 mol/L	σ_2[b] ($\times 10^{-20}$ cm^4/GW)	σ_2'[b] ($\times 10^{-48}$ cm^4·sec ph·molecule)	σ_2'/MW[b] ($\times 10^{-50}$ cm^4·sec·mole ph·molecule·g
AF-350 (1305.76)	349−352	16	400	13.5	96	238	18.2
			[485][c]	(0.064)[e]	(0.53)[e]	(1.32)[e]	(0.10)[e]
AF-380 (1077.47)	307−309	19	428 [485][c]	12.0 (0.047)[e]	92 (0.39)[e]	228 (0.97)[e]	21.2 (0.090)[e]
AF-450 (1916.94)	121−122	44	415.5 [505; 0.47][d]	19.2 (0.066)	159 (0.55)	395 (1.37)	20.6 (0.071)
AF-455 (1916.94)		44	410 [500; 0.48][d]	16.1 (0.061)	134 (0.51)	333 (1.27)	17.4 (0.066)
AF-457 (1315.72)	236−238	23	414 [518; 0.47][d]	13.5 (0.054)	112 (0.45)	278 (1.12)	21.1 (0.085)

[a] All optical data were obtained in THF. The concentrations of all chromophore solutions for nanosecond nonlinear transmission measurements and femtosecond degenerate WLC measurements were set at 0.020 M. [b] Nanosecond values measured at 800 nm; femtosecond values ~790 nm are in parentheses. [c] Excitation wavelength = 390 nm. [d] Quantum efficiency (Φ_f) at room temperature was determined with coumarin 153 ($\Phi_f = 0.495$) as the reference. [e] From ref 15a.

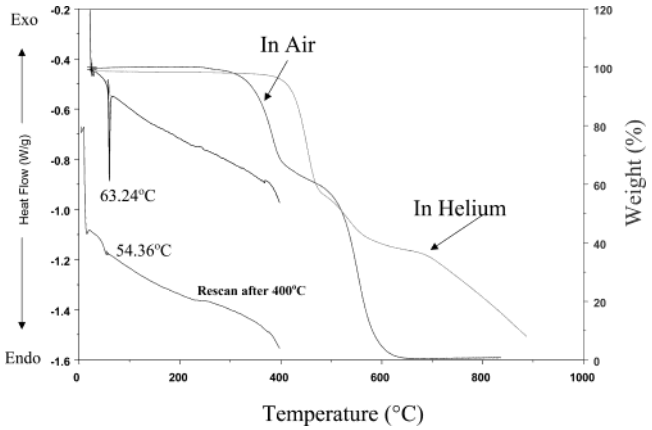

Figure 6. DSC scans (10 °C/min) and TGA results (10 °C/min) in air and helium for **AF-455**.

and σ_2' divided by molecular weight. The latter is most useful with regards to material selection when the maximal number density of a chromophore is required.

Although the central core of the 1,3,5-triazine-based chromophores is more planar than that of **AF-350** and **AF-380**, which should lead to a higher degree of π-delocalization and a relative bathochromic shift in the linear absorption, we note that the maxima of their linear absorption (410−415.5 nm) fall between those of **AF-350** (λ_{max} = 400 nm) and **AF-380** (λ_{max} = 428 nm). A plausible explanation is that the 1,3,5-substitution pattern of the triazine core does not promote strong π-interactions among the three branches. When they were excited at 410 nm, they underwent one-photon emission processes with the maximal at wavelengths 500−518 nm and approximately the same quantum efficiency (Φ_f = 0.47−0.48 with reference to coumarin 153, Φ_f = 0.495).

All three 1,3,5-triazine-based AFX chromophores have effective two-photon cross-section (σ_2') values comparable to or higher than those for **AF-350** and **AF-380** at 800 nm in the nanosecond regime (Table 1). Although the chromophoric core of the three 1,3,5-triazine-based AFX chromophores is the same, the architecture of the alkyl chains has a dramatic effect on the effective σ_2'. Whereas **AF-450** and **AF-455** have almost twice the weight percent of alkyl groups than **AF-457**, their effective σ_2' values are 42% and 20% larger than that of the latter. On the basis ofthe results of a previous study on the molecular environment effect (i.e., length of alkyl side-chains and solvent polarity) on the two-photon absorption of selected AFX chromophores,[32] this observation can be attributed to the nonpolar molecular environment created by the long alkyl chains of **AF-450** and **AF-455** and its stabilization of the excited state (i.e., longer lifetime) by hampering the interactions and collisions with the more polar solvent molecules and thus, enhancing the excited-state absorption processes that contribute to the effective nanosecond cross-sections. The observed trend in the relative fluorescence intensity, **AF-455** > **AF-450** > **AF-457** appears to support this argument (see Figure 7). Another noteworthy observation is that **AF-455**'s nanosecond cross-section value is almost 19% less than that of **AF-450**. Within the experimental uncertainty (±15%), this disparity *may be* significant in the view that they are structural isomers. The only difference between them is the fact that **AF-455** is a mixture of stereoisomers whereas **AF-450** is a pure compound. We suspect that the branching of the alkyl chains in **AF-455** may amplify the local steric effect around the chromophoric unit leading to some conformational changes that interfere with the efficiency of π-delocalization and photoinduced intramolecular charge-transfer processes. This is consistent with the slight hypsochromic (blue) shift (~5.5 nm) in the linear absorption band of **AF-455**.

Degenerate Two-Photon Absorption Spectra. As noted in our previous papers,[7] we reiterate that valid structure/property relationships based on the comparisons of two-photon absorption cross-sections at a single

(27) Gujadhur, R.; Venkataraman, D.; Kintigh, J. T. *Tetrahedron Lett.* **2001**, *42*, 4791−4793.

(28) Qualitative wave-guiding property was demonstrated as follows: when a light source was focused on one end of a short, drawn fiber (L ~6 mm and D ~35 um) in a dark room, the opposite end of the fiber behaves like a light bulb as viewed under a microscope.

(29) He, G. S.; Yuan, L.; Cheng, N.; Bhawalkar, J. D.; Prasad, P. N.; Brott, L. L.; Clarson, S. J.; Reinhardt, B. A. *J. Opt. Soc. Am. B* **1997**, *14*, 1079−1087.

(30) Boggess, T. F.; Bohnert, K. M.; Mansour, K.; Moss, S. C.; Boyd, I. W. *IEEE J. Quantum Electron.* **1986**, *22*, 360.

(31) THF exhibits a relatively weak linear absorption band around 910-nm position as indicated in Figure 7. However, the influence of this residual linear absorption of THF and the reflection from the windows of quartz cuvette could be automatically removed as we did compare a chromophore solution in THF to a pure THF sample for each TPA measurement procedure.

(32) Baur, J. W.; Alexander, M. D., Jr.; Banach, M.; Denny, L. R.; Reinhardt, B. A.; Vaia, R. A. *Chem. Mater.* **1999**, *11*, 2899−2906.

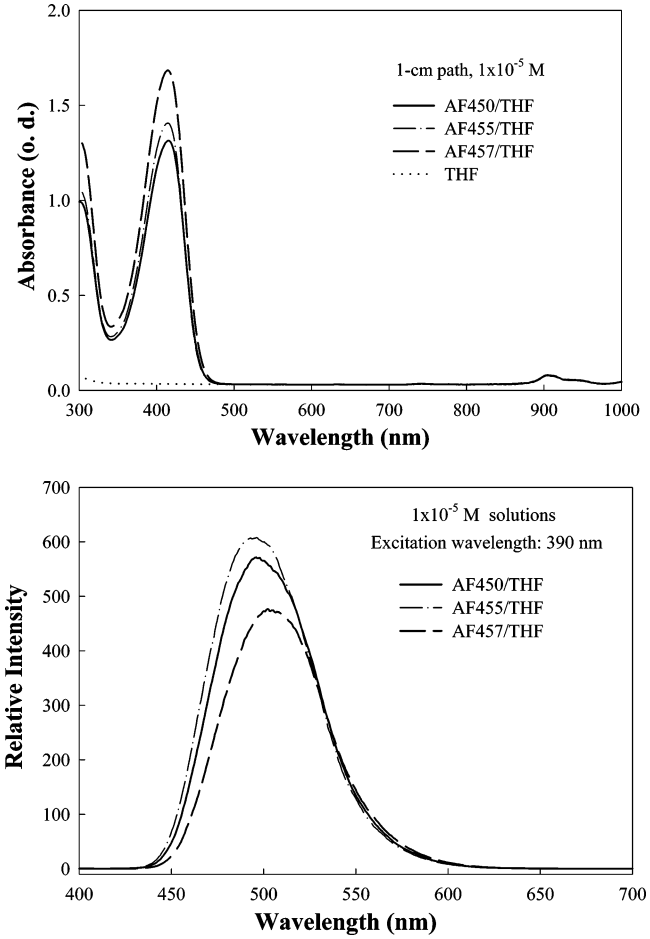

Figure 7. Linear absorption and emission spectra of **AF-450**, **AF-455**, and **AF-457**. [Note that the small absorption band around 900 nm was present in all solutions and is due to the solvent (THF) absorption.]

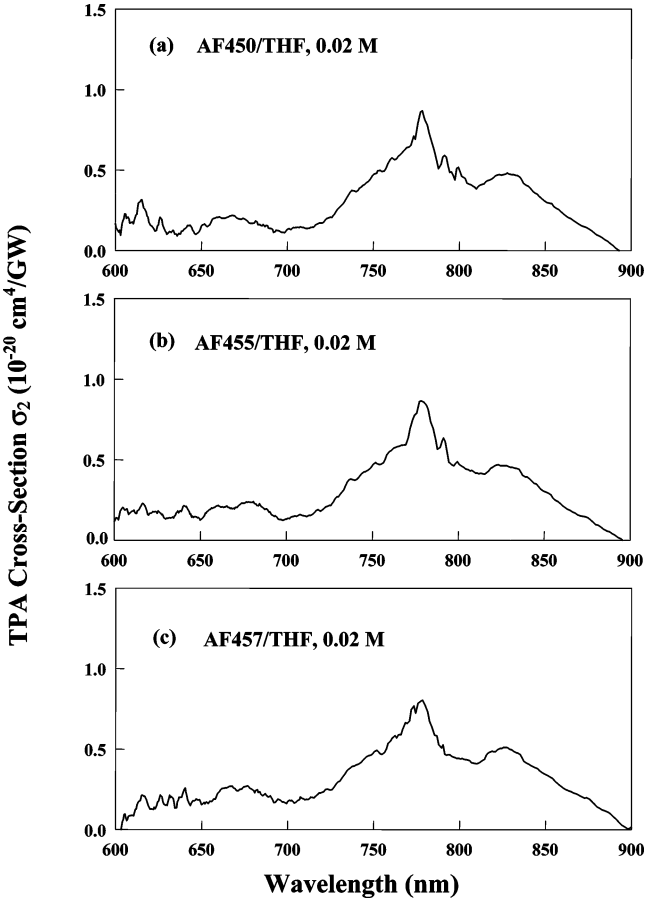

Figure 8. Two-photon spectra for **AF-450**, **AF-455**, and **AF-457**.

wavelength can only be ascertained for those molecules that have their two-photon absorption peak at approximately the same wavelength. If the two-photon peak is shifted away from the experimental wavelength of 800 nm, comparisons of absolute cross-sections are misleading. Furthermore, it should also be pointed out that the measured values represent "effective" cross-sections.[33] Nanosecond excitations are not sufficient for ascertaining the contribution of excited-state absorption from that of instantaneous two-photon absorption. Thus, femtosecond two-photon absorption spectra are required.

Figure 8 shows the measured TPA cross-section values as a function of excitation wavelength, obtained by using a single femtosecond white-light continuum generation beam and the direct degenerate-TPA measurement technique. The continuum was generated in a 10-cm heavy water cell pumped by ~790-nm and ~150-fs laser pulses at 1-kHz repetition rate. The underlying principle and technical details of this new TPA spectral measurement technique have been previously described.[15b,34] Qualitatively, the shape, position, and intensity of the TPA bands for these chromophores are quite similar. The intrinsic TPA cross-section values at ~790 nm for **AF-450**, **AF-455**, and **AF-457** are $\sigma_2 =$ 0.55, 0.51, and 0.45 (±15%) $\times 10^{-20}$ cm^4/GW, ($\sigma_2' =$ 159, 134, and 112 GM), in that order. These values are comparable to that of **AF-350** (see Table 1) measured at the same wavelength. However, their TPA peaks are all located at ~779 nm, and the corresponding TPA cross-section values are considerably higher: $\sigma_2 = 0.87$, 0.86, and 0.80 (±15%) $\times 10^{-20}$ cm^4/GW, ($\sigma_2' =$ 216, 214, and 199 GM), in that order for **AF-450**, **AF-455**, and **AF-457**. Consistent with numerous reports, TPA cross-section values obtained with femtosecond laser excitation from solutions with the same concentration (0.02 M), path length (1 cm), and laser wavelength (~800 nm) are substantially smaller than those obtained from the measurements in nanosecond regime. One possible explanation is that once the input excitation laser pulse-duration has reached femtosecond regime, the role of TPA-induced excited state absorption (ESA) is considerably reduced. ESA is most likely to take place from the fluorescence-emitting state that has a longer lifetime compared to other upper excited states. After two-photon absorption, the chromophore molecules arrive at the higher upper excited state (compared with single-photon excitation and half the wavelength) and then relax to the lower emitting state where ESA can take place under suitable conditions.[15c]

Finally, it is noteworthy that within the accuracy of the technique, the relative peak positions of the prominent TPA bands (**AF-450**, ~779 nm; **AF-455**, ~779 nm; and **AF-457**, ~779 nm) approximately parallel those of

(33) Nonetheless, for many applications that utilize the upconverted fluorescence driven by nanosecond laser pulses, these effective values are useful.

(34) He, G. S.; Lin, T.-C.; Dai, J.; Swiatkiewicz, J.; Prasad, P. N.; Kannan, R.; Vaia, R. A.; Tan, L.-S. *Optics Express* **2002**, *10*, 566.

the linear absorption (**AF-450**, 415 nm; **AF-455**, 410 nm; and **AF-457**, 414 nm). Overall, these observations reaffirm the empirical use of linear absorption spectra to guide AFX design motifs.

Conclusion

The combination of planar 1,3,5-triazine core and diphenylamino endgroups with fluorene π-bridges has resulted in another subset of AFX chromophores with large two-photon cross-sections. Their overall molecular structures (octupoles) are similar to those of **AF-350** and **AF-380** except that the positions of π-donating and π-accepting components are reversed. However, both types of structural motifs are apparently effective in achieving large two-photon responses. In addition, our results show that the concept of incorporating highly branched, solubilizing side groups into the two-photon absorbing structures and in-situ blending can lead to low-melting glassy materials. Although we have yet to achieve the objective of synthesizing a AFX-based two-photon absorbing liquid at room temperature, the fiber-forming property of **AF-455** at relatively low melt temperature is interesting, and its wave-guiding properties suggest a potential usefulness as a nonlinear optical fiber.

Experimental Section

All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured at 270 and 50 MHz on a JEOL-270 NMR spectrometer. Elemental analysis and mass spectral analysis were performed at Systems Support Branch, Materials Directorate, Air Force Research Lab, Dayton, OH. Differential scanning calorimetry (DSC) analyses were performed in nitrogen at a heating rate of 10 °C/min using a Perkin-Elmer model 2000 thermal analyzer equipped with a differential scanning calorimetry cell. Thermogravimetric analyses (TGA) were obtained in helium and air atmospheres with a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer.

I. Preparation of 2,4,6-Tris[7-(diphenylamino)-9,9-didecyl fluoren- 2-yl]-1,3,5-triazine (AF-450). *(a) 2-Bromofluorene.*[35]To a solution of fluorene (16.6 g, 0.1 mol) in propylene carbonate (125 mL) at 60 °C, *N*-bromo succinimide (17.8 g, 0.1 mol) was added in one portion, and the mixture was allowed to cool over a period of 1 h. The solids that separated on dilution with water (2 L) were collected, and dissolved in toluene (250 mL). The toluene solution was washed with water, dried over $MgSO_4$, and subjected to rotary evaporation. The solids that remained after rotary evaporation were recrystallized from ethanol−water, 23.3 g (95% yield), mp 95.6−101.3 °C. MS (*m*/*z*): 322, 324, 326 (M^+ dibromofluorene), 244, 246 (M^+).

(b) 2-Bromo-7-iodofluorene.[36]A mixture of 2-bromofluorene (48.6 g, 0.192 mol), acetic acid (800 mL), water (40 mL), concentrated sulfuric acid (20 mL), iodine (20.4 g, 0.08mol), and iodic acid (8.03 g, 0.046 mol) was heated at 80−90 °C for 2 h, cooled, and filtered. The solids were washed with acetic acid (400 mL) and water (500 mL) to afford the product 62.3 g (87% yield), mp 178−180 °C. MS (*m*/*z*): 370, 372 (M^+). Anal. Calcd. for $C_{13}H_8BrI$: C, 42.08%; H, 2.17%; Br, 21.54%; I, 34.20%. Found: C, 41.90%; H, 2.27%; Br, 21.26%, I, 34.65%.

(c) 2-Bromo-7-iodo-9,9-didecylfluorene. To a mechanically stirred mixture of 2-bromo-7-iodofluorene (41.34 g, 0.11 mol), DMSO (100 mL), potassium iodide (1.7 g), and powdered potassium hydroxide (28 g) cooled in a cold water bath, 1-bromodecane (53 mL) was added dropwise, and the mixture was stirred for 24 h. The oil that separated on dilution with water was extracted with toluene. The toluene extract was washed with water, dried, and concentrated on a rotary evaporator. The residual oil was passed through a column of alumina (300 g). Elution with 900 mL of hexanes gave the product as an oil, 65 g. This oil was left in 200 mL of 2-propanol and the product was solidified, 58.63 g (81% yield), mp 43−45 °C. Recrystallization from 2-propanol raised the mp to 45.6−46.6 °C. MS (*m*/*z*): 650, 652 (M^+). Anal. Calcd. for $C_{33}H_{48}BrI$: C, 60.83%; H, 7.43%; Br, 12.26%; I, 19.48%. Found: C, 61.06%; H, 7.44%; Br, 11.96%; I, 19.18%. ^{1}H NMR ($CDCl_3$; δ in ppm): 0.56−0.60 (br, 4H, CH_2), 0.85 (s, 6H, CH_3), 1.04−1.29 (m, 28H, CH_2), 1.86−1.92 (m, 4H, CH_2), 7.37−7.65 (m, 6H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 14.14, 22.66, 23.61, 29.20, 29.28, 29.51, 29.71,29.86, 31.88, 40.11, 55.57, 76.54, 77.00, 77.49, 92.98, 121.12, 121.46, 121.61, 126.10, 130.10, 132.03, 136.00, 139.03, 139.09, 139.66, 139.72, 152.30, 152.45, 152.68.

(d) (7-Bromo-9,9-didecyl-fluoren-2-yl)diphenylamine. The synthesis of this compound was described previously,[7a] and the present method is a higher-yield alternative. A mixture of 2-bromo-7-iodo-9,9-didecylfluorene (13.7 g, 0.021 mol), diphenylamine (3.4 g, 0.02 mol), potassium carbonate (6.4 g, 0.046 mol), tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1, 1.8 g, 0.06 mol), copper bronze (1.2 g, 0.019 mol), and xylenes (25 mL) was brought to reflux, and xylenes were distilled off to reach a reaction temperature of 175 °C. The reaction was maintained at this temperature for 18 h. Some more solvent was distilled off to reach a reaction temperature of 200 °C, where the reaction was held for an additional 6 h. The mixture was then cooled, diluted with 100 mL of toluene, and filtered. The filtrate was concentrated, and the residue was transferred to a column of 350 g of silica gel. Elution with hexanes gave in the earlier fractions a mixture of dibromo- and bromoiodofluorenes as an oil (0.38 g), and in later fractions, the desired product (11.3 g), which was recrystallized from 2-propanol to afford 10.7 g (77% yield) of pure product, mp 66.3−67.4 °C. MS: 691, 693 (M^+). Anal. Calcd. for $C_{45}H_{58}NBr$: C, 78.01%; H, 8.44%; N, 2.02%; Br, 11.53%. Found: C, 78.08%; H, 8.50%; N, 1.96%; Br, 11.92%. ^{1}H NMR ($CDCl_3$; δ in ppm) 0.62−0.66 (br, 4H, CH_2), 0.86 (t, 6H, CH_3), 0.97−1.30 (m, 28H, CH_2), 1.79−1.85 (m, 4H, CH_2), 6.97−7.51 (m, 16H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 14.11, 22.66, 23.79, 29.29, 29.55,-29.92, 31.88, 40.11, 55.29, 119.08, 120.14, 120.37, 120.43,-122.59, 123.42, 123.88, 125.93, 129.15, 129.87, 135.03, 139.92, 147.50,147.87, 151.70, 152.85.

*(e) 2,4,6-Tris[7-(diphenylamino)-9,9-didecyl fluoren-2-yl]-1,3,5-triazine (**AF-450**).* To a solution of (7-bromo-9,9-didecylfluoren-2-yl)diphenylamine (12.46 g, 18 mmol) in THF (75 mL) cooled in a dry ice acetone bath, *n*-butyllithium (1.6 M solution in hexanes, 12 mL, 19.2 mmol, 1.07 equiv) was syringed in. After 25 min and when the temperature rose to −50 °C, a solution of 2,4,6-trifluoro-triazine (cyanuric fluoride; 0.81 g, 6 mmol) in THF (3 mL) was added. The mixture was left in the cooling bath, was allowed to come to room temperature overnight, and then diluted with water and toluene. The organic phase was dried over magnesium sulfate and concentrated, and the residue was transferred to a column of alumina eluting with 10% toluene−heptane to afford the product as a glassy material. The product solidified on standing in 2-propanol, 6.55 g, (57% yield); mp 121−122 °C. LR-FAB-MS: 1917.4, 1916.41 and 1915.4 amu ($M^+ + 1$). Anal. Calcd. for $C_{138}H_{174}N_6$: C, 86.47%; H, 9.15%; N, 4.38%. Found: C, 86.49%; H, 9.05%; N, 4.35%. ^{1}H NMR ($CDCl_3$; δ in ppm): 0.87 (t, 18H, CH_3), 1.11−1.25 (m, 96H, CH_2), 1.77−2.26 (m, 12H, CH_2), 7.01−7.30 (m, 36H, Ar−C−H), 7.68 (d, 3H, Ar−C−H), 7.83 (d, 3H, Ar−C−H), 8.72 (d, 3H, Ar−C−H), 8.81,8.84 (dd, 3 H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 14.08, 14.31, 22.63, 22.86, 23.96, 29.31, 29.40, 29.60, 30.03, 30.32, 31.88, 32.17, 40.23, 55.20, 118.96, 119.10, 121.24, 122.76, 122.96, 123.08, 123.28, 124.09, 124.23, 128.41, 129.21, 134.51, 135.26, 145.37,

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147.84, 148.07, 150.95, 153.43, 171.75.

II. Preparation of Stereoisomeric Mixture of 2,4,6-Tris [9,9-bis(3,7-dimethyloctyl)-7-(diphenylamino)-fluoren-2yl]-1,3,5-triazine (AF-455). *(a) Racemic Dihydrocitronellyl Bromide (1-Bromo-3,7-dimethyloctane).* Concentrated sulfuric acid (17 mL) was added to 48% hydrobromic acid (100 mL) with stirring, and then racemic 3,7-dimethyloctanol (dihydrocitronellol, Aldrich, 67 mL, 100 g) was added to the mixture. The mixture was then heated to 120−125 °C, and kept at this temperature for 3 h. The reaction was cooled, and extracted into heptane (300 mL). The heptane layer was washed with hydrochloric acid, water, and sodium bicarbonate solution, dried, and concentrated to leave an oil, 81.5 g. This oil was distilled under vacuum at a bath temperature of 120−125 °C to afford the bromide product as an oil, bp 85−87 °C/10 mmHg, 78.2 g, 100% yield. MS (*m*/*z*): 220, 222 (M^+). ^{1}H NMR ($CDCl_3$; δ in ppm): 0.86, 0.88 (d, 6H, CH_3), 0.88,0.90 (d, 3H, CH_3), 1.01−1.89 (m, 10H, CH_2), 3.37−3.47 (m, 2H, CH_2Br). ^{13}C NMR ($CDCl_3$; δ in ppm): 18.98, 22.61, 22.69, 24.56, 27.96, 31.68, 32.14, 36.74, 39.19, 40.11.

(b) Racemeic and Meso 9,9-Bis(3,7-dimethyloctyl)-2,7-dibromofluorene. To a mechanically stirred mixture of 2,7-dibromofluorene (58.32 g, 0.18 mol), potassium iodide (3.0 g, 18 mmol), potassium hydroxide (50.4 g, 0.9 mol), and DMSO (150 mL) cooled in ice−water to 15 °C, dihydrocitronellyl bromide (86.8 g, 0.392 mol) was added, and the mixture was stirred at room temperature for 18 h. The mixture was poured into water, and the product was extracted into a mixture of 1:1 toluene−heptane. The organic phase was washed with water, dried, and concentrated. The residual oil was refluxed with pyridine for 18 h to quaternize any unreacted bromide, the mixture was diluted with toluene−heptane, and the organic phase was washed with water, dried, and concentrated. The residual orange oil was transferred to a column of 1050 g of alumina. Elution with hexanes (1800 mL) gave the product, 102.25 g, 94% yield, as a colorless oil. A sample of this material on storage in the refrigerator solidified. The solids after standing with 2-propanol were collected, mp 48.2−50.8 °C. MS (*m*/*z*): 602, 604, 606 (M^+). Anal. Calcd. for $C_{33}H_{48}Br_2$: C, 65.56%; H, 8.00%; Br, 26.44%. Found: C, 65.80%; H, 7.81%; Br, 26.30%. ^{1}H NMR ($CDCl_3$; δ in ppm): 0.67−0.69 (d, 6H, CH_3), 0.80−0.82 (d, 12 H, CH_3), 0.84−1.10 (m, 18 H, CH_2 and C−H), 1.28−1.64 (m, 2 H, CH), 1.74−2.13 9 m, 4 H, CH_2), 7.40−7.50 (m, 6 H, Ar−C−H0. ^{13}C NMR ($CDCl_3$; δ in ppm): 19.46, 22.60, 22.69, 24.53, 27.90, 30.26, 32.74, 36.48, 37.40, 39.13, 55.46, 121.06, 121.49, 126.07, 130.16, 139.09, 152.45.

(c) Racemic and Meso [9,9-Bis(3,7-dimethyloctyl)-7-bromofluoren-2yl]diphenylamine. A mixture of 9,9-bis(3,7-dimethyloctyl)-2,7-dibromofluorene (56.2 g, 0.093 mol), diphenylamine (7.87 g, 0.0465 mol), bis(dibenzylideneacetone)palladium(0) (0.30 g, 0.52 mmol), bis(diphenylphosphino)ferrocene (0.32 g, 0.58 mmol), sodium *tert*-butoxide (5.4 g, 0.0562 mol), and toluene (330 mL) was kept under nitrogen at 80 °C for 18 h, and then at 100 °C for 5 h. The mixture was cooled and diluted with toluene and water, and the organic phase was washed with water, dried, and concentrated on a rotary evaporator. The residual brown oil, 59 g, was transferred to a column of 600 g of silica gel. Elution with hexanes (1200 mL) resulted in a fraction containing unreacted dibromofluorene, 28.09 g. MS: *m*/*z* 602, 604, 606. The desired product was eluted out with heptane as an oil, 28.49 g, 88.5% yield. MS (*m*/*z*): 691, 693 (M^+). Anal. Calcd. for $C_{45}H_{58}NBr$: C, 78.01%; H, 8.44%; N, 2.02%; Br, 11.53%. Found: C, 78.13%; H, 8.47%; N, 2.09%; Br, 11.74%. ^{1}H NMR ($CDCl_3$; δ in ppm): 0.69−0.70 (d, 6H, CH_3), 0.81, 0.83 (dd, 12H, CH_3), 0.85−1.11 (m, 18H, CH_2 and C−H), 1.28−1.60 (m, 2H, C−H), 1.69−2.03 (m, 4H, CH_2), 6.84−7.52 (m, 16H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 19.47, 19.67, 22.57, 22.69, 22.84, 22.98, 24.56, 24.76, 27.85, 28.13, 30.44, 30.67, 32.83, 33.12, 36.63, 36.83, 37.29, 37.61, 39.13, 39.19, 55.12, 118.99, 120.14, 120.37, 120.43, 122.56, 123.51, 123.83, 124.03, 124.11, 124.23, 125.84, 129.155, 129.44, 129.87, 135.17, 139.98, 147.50, 147.84, 148.13, 151.59, 152.74.

*(d) Stereoisomeric Mixture of 2,4,6-Tris [9,9-bis(3,7-dimethyloctyl)-7-(diphenylamino)-fluoren-2yl]-1,3,5-triazine (**AF-455**).* To a solution of [9,9-bis(3,7-dimethyloctyl)-7-bromofluoren-2yl]diphenylamine (24.9 g, 36 mmol), in THF (150 mL), cooled in a dry ice−acetone bath, a solution of *n*-butyllithium in hexanes (1.6 M, 24 mL, 38.4 mmol) was added, and after 25 min a solution of 1,3,5-trifluorotriazine (cyanuric fluoride; 1.62 g, 12 mmol) in THF (100 mL) was added. The mixture was allowed to come to room temperature, and then diluted with toluene and water. The organic phase was washed with water, dried, and concentrated. The residue was chromatographed over 700 g of alumina. The product was eluted with 10% toluene−heptane and isolated in two fractions, 4.7 g, and 7.05 g, as yellow glassy materials, 51% yield. The sample solidified on storage, and the solid melted over the range 67−72 °C on a melt-temp apparatus. DSC shows a small melting endotherm at 63.24 °C and glass-transition temperature at 54.36 °C on a second heating scan. FAB-MS (*m*/*z*): M^+ at 1917.31. Anal. Calcd. for $C_{138}H_{174}N_6$: C, 86.47%; H, 9.15%; N, 4.38%. Found: C, 86.66%; H, 9.20%; N, 4.25%. ^{1}H NMR ($CDCl_3$; δ in ppm): 0.74, 0.77 (d, 36H, CH_3), 0.78, 0.79 (d, 18H, CH_3), 0.84−1.13 (m, 54H, CH_2 and C−H), 1.35−1.50 (m, 6H, C−H), 1.88−2.24 (m, 12H, CH_2), 7.00−7.30 (m, 36H, Ar−C−H), 7.66−7.84 (q, 6H, Ar−C−H), 8.70 (s, 3H, Ar−C−H), 8.78−8.81 (d, 3H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 19.47, 19.73, 22.55, 22.66, 24.65, 24.79, 27.88, 30.64, 30.87, 32.89, 32.94, 36.77, 36.92, 37.46, 37.52, 37.64, 39.19, 55.03, 118.84, 119.05, 121.21, 122.73, 123.05, 123.31, 123.37, 124.09, 124.46, 128.32, 129.21, 134.68, 135.43, 145.31, 147.84, 148.05, 150.81, 153.23, 171.80.

III. Preparation of 2,4,6-Tris[(7-(diphenylamino)-9,9-diprop-2-enylfluoren-2-yl]-1,3,5-triazine (AF-457). *(a) 2-Bromo-7-iodo-9,9-diprop-2-enylfluorene.* To a mixture of 2-bromo-7-iodofluorene (129.5 g, 0.25 mol), obtained by iodination of 2-bromofluorene, potassium hydroxide (118.0 g, 2.1 mol), potassium iodide (7.0 g, 0.042 mol), and DMSO (500 mL), allyl bromide was added dropwise at 15−20 °C. The mixture was stirred for 18 h and poured into 4 L of water. The separated solids were collected, washed with water, and dried, 155.48 g, mp 146.7−150.5 °C. This crude product was heated to reflux in 500 mL of ethanol for 2 h, cooled, and filtered. The solids were washed with ethanol, 146.5 g, mp 149.4−151.8 °C, 93% yield. A portion was recrystallized twice from hexanes, mp 153.4−154.0 °C. MS (*m*/*z*): 450, 452 (M^+). Anal. Calcd. for $C_{19}H_{16}BrI$: C, 50.58%; H, 3.57%; Br, 17.71%; I, 28.13%. Found: C, 50.93%; H, 3.70%; Br, 17.41%; I, 27.88%. ^{1}H NMR ($CDCl_3$; δ in ppm): 2.65 (d, 4H, CH_2), 4.75−4.87 (m, 4H, C=CH_2), 5.15−5.22 (m, 2H, C=CH), 7.43−7.52 (m, 6H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 43.14, 54.66, 76.54, 77.00, 77.49, 118.50, 121.21, 121.26, 126.94, 130.48, 132.52, 138.66, 151.10.

(b) 2-Bromo-7-(diphenylamino)-9,9-diprop-2-enylfluorene. A mixture of 2-bromo-7-iodo-9,9-diprop-2-enylfluorene (4.5 g, 10 mmol), diphenylamine (1.91 g, 11.3 mmol), toluene (125 mL), cesium carbonate (4.89 g, 15.0 mmol), and tris(triphenylphosphine)copper(I) bromide (1.90 g, 2.0 mmol) was heated to reflux, and held at 110−112 °C for 76 h. The reaction was cooled and filtered, and the solids were washed with toluene. The toluene filtrate was washed with water, dried, and concentrated. The residue was chromatographed over silica gel, and the column was eluted with hexanes. Early fractions gave the starting bromoiodofluorene (30%), and later fractions, the desired product, which was recrystallized from 2-propanol, 2.82 g (57% yield), mp 127−129 °C. Another recrystallization raised the mp to 130.1−131.2 °C. MS (*m*/*z*) 491, 493 (M^+). Anal. Calcd. for $C_{31}H_{26}BrN$: C, 75.61%; H, 5.32%; N, 2.84%; Br, 16.23%. Found: C, 75.45%; H, 5.55%; N, 2.81%; Br, 16.29%. ^{1}H NMR ($CDCl_3$; δ in ppm): 2.50−2.62 (m, 4H, CH_2), 4.74−4.84 (m, 4H, C=CH_2), 5.14−5.27 (m, 2H, C=CH), 6.96−7.69 (m, 16H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 43.28, 54.31, 54.40, 76.51, 76.97, 77.43, 91.20, 117.95, 119.77, 119.85, 119.91, 120.49, 120.86, 122.62, 123.68, 123.74, 123.86, 124.29, 126.62, 129.13, 129.56, 130.22, 132.47, 133.07, 134.51, 136.09, 139.55, 140.15, 147.35, 147.50, 147.73, 150.09, 150.26, 151.27, 151.47.

*(c) 2,4,6-Tris[(7-(diphenylamino)-9,9-diprop-2-enylfluoren-2-yl]-1,3,5-triazine (**AF-457**).* To a solution of 2-bromo-7-(diphenylamino)-9,9-diprop-2-enylfluorene (22.16 g, 0.045 mol) in THF (200 mL), cooled in a dry ice−acetone bath, a solution of

n-butyllithium in hexanes (1.6 M, 30 mL, 0.048 mol), was added by syringe over 5 min. After 25 min, over a 30-minute period, a solution of cyanuric fluoride (2.025 g, 0.015 mol) in THF (100 mL) was added to result in a greenish fluorescent solution, which turned orange at the end of additon. The mixture was allowed to warm slowly to room temperature, diluted with toluene and water, and the organic phase was dried and concentrated. The residue was chromatographed over alumina (eluted with 1:3 toluene−heptane), rechromatographed over silica gel (eluted with 1:3 toluene−heptane), and then crystallized from 1:3 toluene−heptane. The desired product was obtained as a bright yellow solid, 11.84 g, 60% yield, mp 235−237 °C. Recrystallization from 2:1 heptane−toluene raised its mp to 236−238 °C. MS: *m*/*z* 1314 (M^+). Anal. Calcd. for $C_{96}H_{78}N_6$: C, 87.64%; H, 5.90%: N, 6.3%. Found: C, 87.59%; H, 6.06%; N, 6.15%. ^{1}H NMR ($CDCl_3$; δ in ppm): 2.65−2.90 (m, 12H, CH_2), 4.82−4.93 (m, 12H, C=CH_2), 5.30−5.45 (m, 6H, C=CH), 7.08−7.30 (m, 36H, Ar−C−H), 7.65−7.84 (dd, 6H, Ar−C−H), 8.81−8.84 (m, 6H, Ar−C−H). ^{13}C NMR ($CDCl_3$; δ in ppm): 43.51, 54.40, 76.54, 77.00, 77.46, 117.89, 119.25, 119.80, 121.32, 122.82, 123.63, 123.80, 124.14, 128.75, 129.24, 133.59, 134.45, 134.77, 144.96, 147.76, 147.99, 149.51, 151.96, 171.60.

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