Diphenylaminofluorene-Based Two-Photon-Absorbing Chromophores with Various π-Electron Acceptors

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A new series of linear, asymmetrical diphenylaminofluorene-based chromophores (**AFX**) with various strong π-electron acceptors were synthesized and evaluated for two-photon absorptivity. These chromophores were studied to determine a suitable replacement for 2-(4-vinyl)pyridine, the π acceptor for our previously reported **AFX** series, which contains a photochemically and thermo-oxidatively unstable olefinic unit. In addition to the benzoyl group (**AF-370**), these π-electron acceptors include 2-benzothiazolyl (**AF-240**), 2-benzoxazolyl (**AF-390**), 2-(*N*-phenyl)benzimidazolyl (**AF-386**), and 2-(3,4-diphenyl)imidazolyl (**AF-385**) moieties (five-membered heterocycles) and the 2-quinoxalinyl (**AF-260**) group (six-membered heterocycle). From nanosecond nonlinear transmission measurements, these new chromophores have effective two-photon cross sections (σ_2') at 800 nm, spanning from 3.87×10^{-48} cm^4 s/(photon molecule) for **AF-385** to 97.46×10^{-48} cm^4 s/(photon molecule) for **AF-240**. Two of them, 2-benzothiazolyl-end-capped **AF-240** and benzoyl-containing **AF-370** [$\sigma_2' = 84.32 \times 10^{-48}$ cm^4 s/(photon molecule)] stand out as having relatively good, albeit lower, values of two-photon cross sections, as compared to that of previously reported *N*,*N*-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-didecyl-fluorene-2-amine, **AF-50** [$\sigma_2' = 115.6 \times 10^{-48}$ cm^4 s/(photon molecule)]. However, we observed that **AF-240** was more photochemically robust than **AF-50** when their THF solutions were subjected to repetitive and prolonged exposure to nanosecond laser radiation. Finally, on the basis of our nanosecond TPA cross-section data (σ_2'/MW values), the general trend for π-electron accepting ability, i.e., ability to accept charge transferred from diphenylamine appears to be as follows: 2-(4-vinyl)pyridine > 2-benzothiazolyl > benzoyl > 2-(N-phenylbenzimidazolyl > 2-quinoxalinyl > 2-benzoxazolyl > 2-(4,5-diphenyl)imidazoyl.

Introduction

Two-photon or multiphoton absorption occurs through the simultaneous absorption of two or more photons via virtual states in an absorbing medium, with the former being more common. For a given chromophore, these absorption processes take place at wavelengths that are much longer than the cutoff wavelength of the chromophore's linear (single-photon) absorption. In the case of two-photon absorption (TPA) process, two quanta of photons can be absorbed from a single light source (degenerate TPA) or from two sources of different wavelengths (nondegenerate TPA). Although multiphoton absorption processes have been known since 1931,[1] this field remained dormant largely because of the lack of TPA-active materials with sufficiently large cross sections. In the mid-1990s, several new classes of chromophores exhibiting very large effective TPA cross-section (σ_2') values were reported from our[2] laboratories and other groups.[3] In conjunction with the increased availability of ultrafast high-intensity lasers, not only has the renewed interest sparked a flurry of activities in the preparation of novel dye molecules with enhanced

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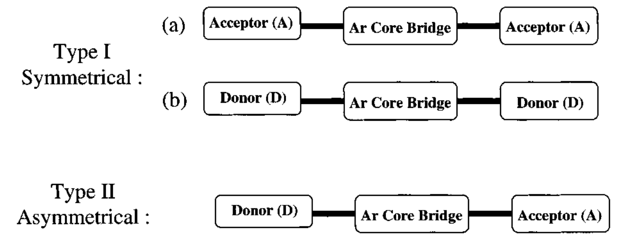

Figure 1. Molecular-structure motifs for highly active two-photon absorbing chromophores.

σ_2' values,[4] but also many previously conceived applications based on TPA process in photonics and biophotonics are now enabled by these new chromophores. It is important to recognize the following features of two-photon materials technology: (a) upconverted emission, whereby an incident light at lower frequency (energy) can be converted to an output light at higher frequency, for instance, IR to UV−vis upconversion; (b) deeper penetration of incident light; (c) highly localized excitation allowing for precision control of in situ photochemical events in the absorbing medium, thereby minimizing undesirable activities such as photodegradation or photobleaching; and (d) fluorescence, when properly manipulated, that allows for information feedback. It is anticipated that further ingenious utilization of these basic characteristics will lead to practical applications other than those that have already emerged in such diverse areas[5] as fluorescence imaging, data storage, eye and sensor protection, microfabrication of microelectromechanical systems (MEMS), and photodynamic therapy.

In our previous work[2], we proposed two general molecular-structure designs (see Figure 1) for augmented TPA responses in one-dimensional molecular systems, namely, symmetrical (type Ia) and asymmetrical (type II). Independently, Perry, Marder, and co-workers[3] also identified similar design criteria for symmetrical structures (both type Ia and type Ib) based on the observation of the effect of strong donors and acceptors on stilbene, *p*-phenylenevinylene (PPV) oligomers and their electronically modified derivatives. In addition to fine-tuning these design concepts, we have synthesized various structures with asymmetrical diphenylaminofluorene as the basic structural motif and 2-(4-vinylpyridyl) as the π acceptor to probe the changes in TPA properties with respect to the following structural variations: (i) nature of aromatic bridging groups, (ii) conjugation length, (iii) coplanarity, and (iv) alkyl chain length. More recently, we have demonstrated the concept of multidimensional conjugation as an approach to further enhancing the cross sections of TPA molecules.[6] We note that a variation of this concept using dendrimeric structures has also been pursued by other research groups.[7,8]

Among the asymmetrical (type II) dyes previously reported, the most active is *N*,*N*-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-*n*-decylfluorene-2-amine (designated as AF-50).[2,9] It incorporates an easily polarizable olefinic double bond directly connected to the π-accepting pyridine end-group. Although it greatly increases the TPA cross section of chromophores, this olefinic bond has limited thermal and photochemical stability, thus reducing the range of the chromophore's utility. In fact, we have observed that some of our vinylpyridine-containing chromophores, including AF-50, are unstable in solution upon exposure to light for a prolonged period of time.[10] Apart from being capable of undergoing rapid photochemical changes,[11] vinylpyridines can undergo Michael addition. As a result, there is a potential for hydration and subsequent retro-aldol cleavage, that is, when water is added, the resultant adduct can break down to an aldehyde and a methyl-substituted heterocycle.

To address the requirement for longer service lifetimes for the TPA chromophores under prolonged and repetitive exposure to high-intensity lasers, we envision the need to produce dyes with increased thermal, chemical, and photochemical stabilities, while maintaining the same level of two-photon response.

Our initial molecular design concept focused on enhancing the effective molecular two-photon absorption cross section at the useful two-photon absorption frequency of the absorbing medium. At the molecular level, structural elements that increase the effective conjugation length and polarizability of the molecule should also increase the two-photon absorption cross section. However, lengthening the conjugation path without compromising coplanarity invariably results in bathochromic shifts of the linear absorption, which, in turn, also shift the two-photon absorption peak. Thus, for certain

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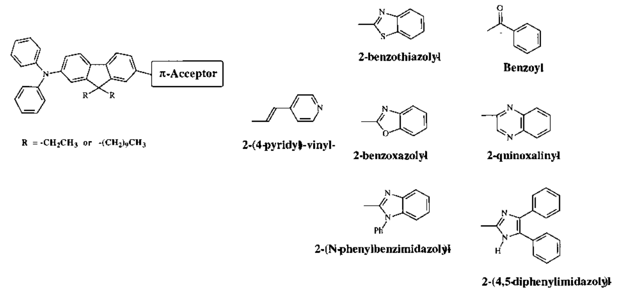

Figure 2. Diphenylaminofluorene-based chromophores with selected π acceptors.

Air Force applications, the major molecular design challenge is to increase the molecular two-photon cross section without shifting the two-photon absorption peak away from 800 nm.

With these considerations in mind and in our continuing effort to further improve the effective TPA cross sections, as well as the photochemical and thermal stabilities, of diphenylaminofluorene-based chromophores, using AF-50 [where the π-accepting component is 2(4-vinyl)pyridyl] as the TPA benchmark at 800 nm in the nanosecond regime, we decided to investigate the suitability of a selected group of π acceptors, as listed in Figure 2, without olefinic bonds but with the same effective conjugation length of the bridge.

Results and Discussion

From the standpoints of design and synthesis, the selection of these π-electron-accepting end-groups were based primarily on the following practical considerations: (i) the accessibility of the intermediates based on the synthetic chemistry developed in our earlier work, namely, (7-bromo-9,9-dialkylfluoren-2-yl)diphenylamines and 2-(9,9-diethyl-7-bromo-2-fluorenyl)benzothiazole, and (ii) the ease in converting the end groups into the heterocyclic π-electron acceptors and benzoyl group.

Aside from the simple benzoyl group, the heterocyclic moieties were chosen primarily for their known (i) strong electron-demanding capabilities;[12] (ii) comparatively better chemical, thermal, thermooxidative, and photochemical stabilities; and (iii) good to excellent fluorescence properties. Furthermore, because maximal coplanarity is critical for efficient charge transfer in a chromophore molecule, we also considered the steric interactions of the heterocyclic end-groups with the 9,9′-diethylfluorene bridge. As is well-established, the merit of an ethylenic bridge is due to its effectiveness not only in increasing the conjugation length, but more importantly, also in facilitating coplanarity when it links two six-membered rings. The directly bonded phenyl groups, for example, are not coplanar because of the steric interactions of the ortho-hydrogens. Therefore, in avoiding steric effects similar to those we examined in linkages of fluorene with the π acceptors, we considered mostly the five-membered heterocycles, such as benzothiazole, benzoxazole, and benzimidazole. In the case of latter, we recognized the fact that a strong intermolecular hydrogen bonding in imidazoles could lead to a solubility problem during TPA characterization. For this reason, we chose *N*-phenylbenzimidazole and 3,4-diphenylimidazole instead of the parent heterocycles.

Chromophore Synthesis. The synthesis of **AF-240**[26] is depicted in Figure 3. The precursor to **AF-240**, 2-(7-bromo-9,9-diethylfluoren-2-yl)benzothiazole (**5**)**,** was prepared in three steps starting from 2,7-dibromofluorene (**1**), as previously reported.[13] On copper-catalyzed amination[14] with diphenylamine in the presence of 18-crown-6 and potassium carbonate, it was transformed to **AF-240** in 46% yield.

As depicted in Figure 4, **AF-260**, **-370**, and **-390** were made from a common intermediate, namely, (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (**3**), whose preparation we have previously reported.[2] Earlier, we prepared this amine by a palladium-catalyzed amination[15] of 2,7-dibromo-9,9-diethylfluorene (**2**) with diphenylamine in low yields when tri-*o*-tolyl phosphine was used as the ligand for palladium (see Figure 3). However, in this work, we used a new synthetic sequence with higher overall yield to prepare the amine intermediate. Thus, fluorene was first ethylated to the known 9,9-diethylfluorene (**7**)[16] in 94% yield. Subsequent monobromination[17] of 9,9-diethylfluorene with *N*-bromosuccinimide in propylene carbonate afforded 2-bromo-9,9-diethylfluorene (**8**) in 90% yield. Iodination of the monobromo intermediate with iodic acid as the reoxidant furnished 2-bromo-7-iodo-9,9-diethylfluorene (**9**) in 79% yield. Finally, copper-catalyzed amination[14] of the bromoiodofluorene furnished (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (**3**) in 67% yield.

The 2-quinoxaline-end-capped chromophore, **AF-260** was obtained in 42% yield in a Stille coupling reaction[18] between 2-iodoquinoxaline[19] and the tri-*n*-butyltin derivative (**10**) of (7-bromo-9,9-diethylfluorene-2-yl)diphenylamine (**3**) by bromide−lithium metathesis with *n*-butyllithium, followed by reaction with tri-*n*-butyltin chloride. The lithio derivative of (7-bromo-9,9-diethylfuorene-2-yl)diphenylamine (**3**), on reaction with benzonitrile followed by acidic hydrolysis of the product, afforded the benzoyl-end-capped **AF-370** in 86% yield. Direct arylation[20] of benzoxazole by the same bromofluorenylamine with the aid of a palladium(0)/Cu(I) catalyst system gave 2-benzoxazolyl-end-capped **AF-390** in 65% yield.

The syntheses of **AF-385** and **AF-386** utilized another common diphenylaminofluorenyl aldehyde intermediate, i.e., 7-(diphenylamino)-9,9-didecylfluorene-2-carboxaldehyde (**12**) (see Figure 5). This aldehyde was derivatized from 7-bromo-9,9-didecylfluoren-2-yl-diphenylamine (**11**), whose synthesis has been described previously.[2] Thus, the halogen−metal exchange reaction of

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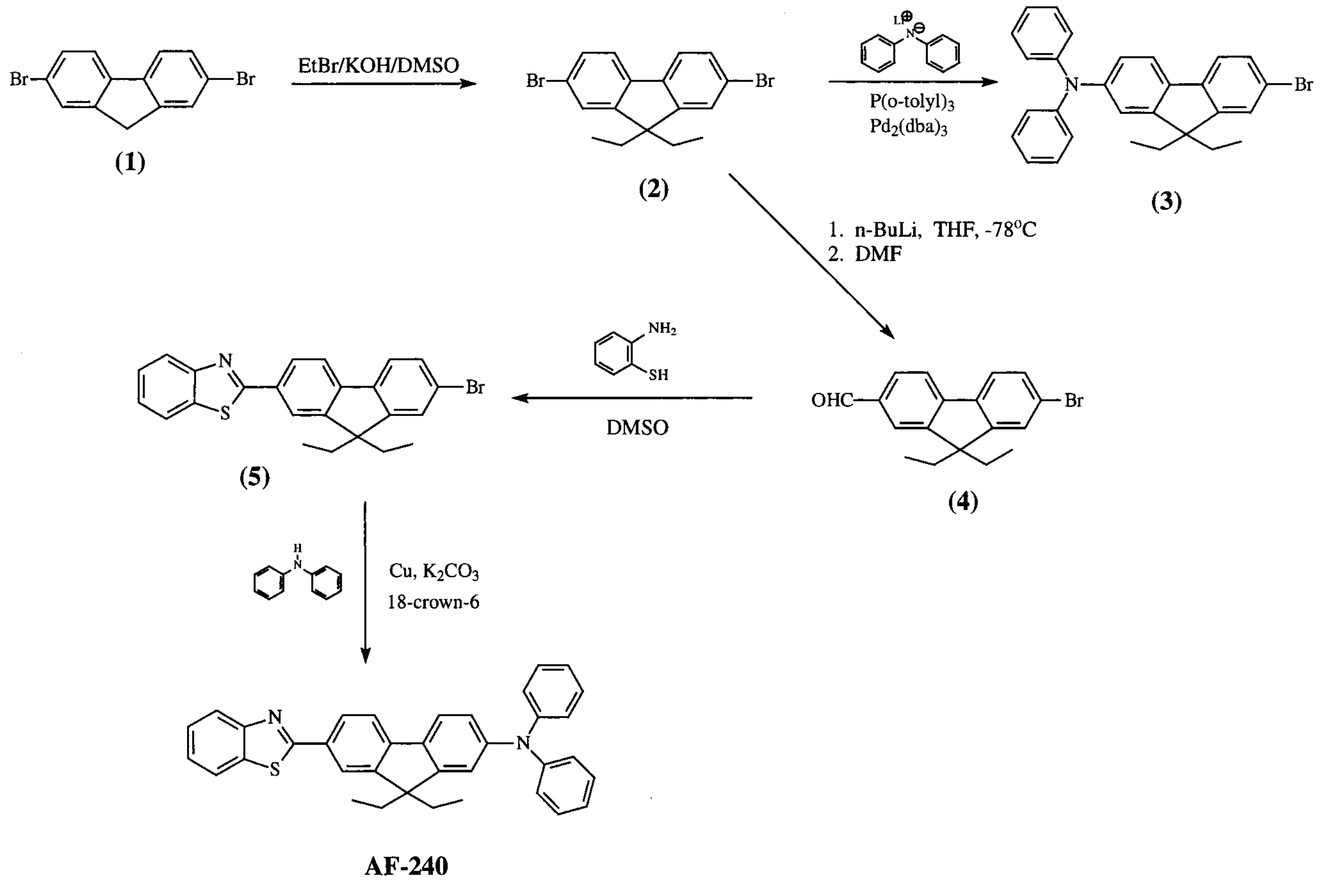

Figure 3. Synthesis of TPA chromophores containing benzothiazolyl acceptor.

this bromo compound with *n*-butyllithium, followed by reaction with DMF and acidic aqueous workup, produced the corresponding aldehyde in 88% yield. The resulting aldehyde, on reaction with benzil and ammonium acetate in acetic acid,[21] led to the isolation of the 3,4-diphenylimidazole derivative (**AF-385**) in 93% yield. The same aldehyde, on reaction with *N*-phenyl-1,2-phenylenediamine, followed by oxidation of the “Schiff's base” intermediate with copper acetate, produced the respective *N*-phenylbenzimidazole chromophore (**AF-386**) in 12% yield.

Solution Characterization of Two-Photon Properties. These organic two-photon materials have strong linear absorption bands around 384–403 nm but no absorption in the spectra ranging from ~480 to ~1150 nm. Therefore, upon radiation with a laser at ca. 800 nm, there should be no linear absorption-induced fluorescence emission. The two-photon energy of ~800-nm IR radiation falls in the strong absorption band of all solutions of these dyes. Very strong frequency upconverted fluorescence emission can be easily observed from these solutions excited even with an unfocused Q-switched near-IR laser beam at the wavelength mentioned above. This indicates that a strong two-photon absorption process producing efficient emission is occurring within the samples. Representative linear absorption and emission spectra of these chromophores are shown in Figure 6. Several methods can be used to investigate the two-photon resonance and determine the two-photon absorption cross section.[2] The nonlinear transmission technique that was adopted for use in this study is direct and very convenient. This technique involves the measurement of the transmitted intensity as a function of the incident intensity. The definitions of relevant key parameters, such as nonlinear absorption coefficient (β) and molecular TPA cross section (σ_2'), and their experimental determinations are described in our previous papers.[6,22,23] It should also be pointed out that inherent in the NLT measurement is the assumption that the two-photon absorption is the predominant process causing the observed intensity-dependent nonlinear absorption. However, as many researchers have indicated, the strong TPA process might considerably increase molecular populations in excited states; thus a secondary process, i.e., the cascaded one-photon absorption from the excited states, might create an additional contribution to the observed nonlinear absorption of the input laser beam. The TPA cross section is commonly used as a parameter to compare the relative magnitude of TPA-dominated nonlinear absorptivity or TPA/excited state absorption combined nonlinear absorptivity among various nonlinear media.[24] Because we cannot simply separate these two contributions through the NLT measurement, we choose to use term “effective TPA cross section” to describe the σ_2' values for AFX chromophores in this paper.

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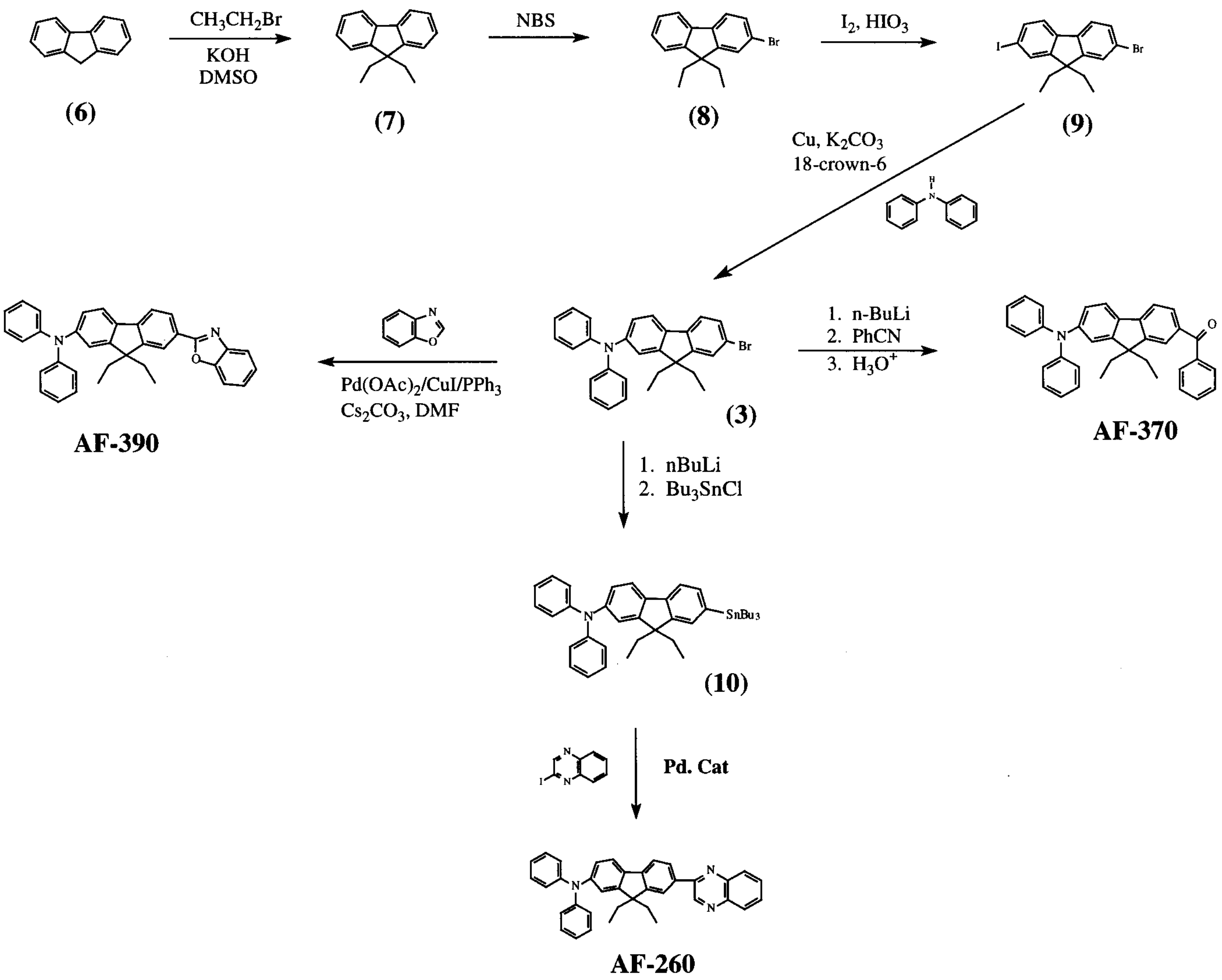

Figure 4. Syntheses of TPA chromophores containing benzoxazolyl, benzoyl, and quinoxaline acceptors.

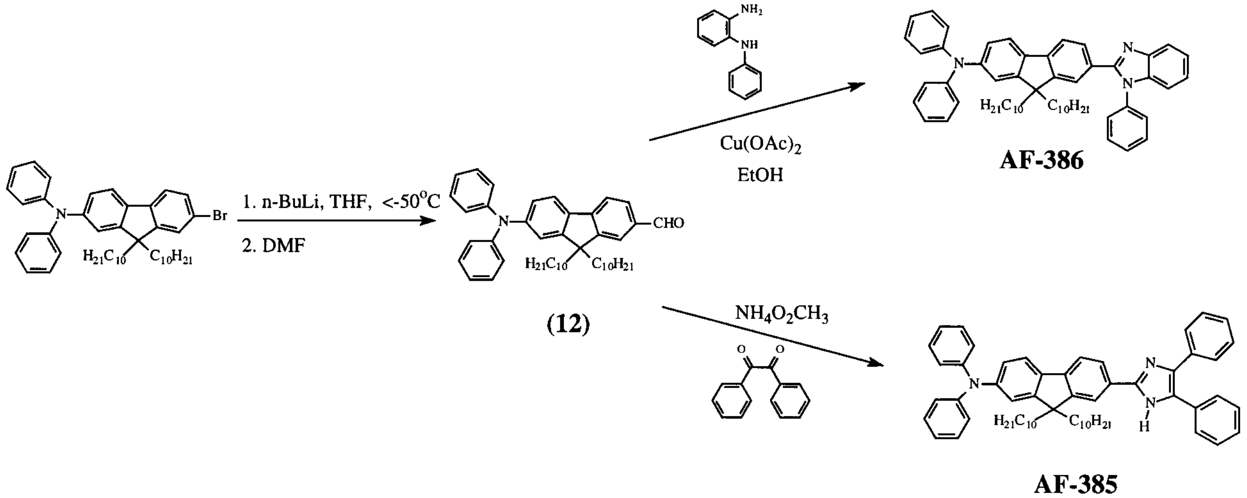

Figure 5. Syntheses of TPA chromophores containing 3,4-diphenylimidazolyl and *N*-phenylimidazolyl π acceptors.

In our measurement, the incident radiation was a linearly polarized ~800-nm pulsed beam, provided by a dye laser system pumped with a frequency-doubled and Q-switched Nd:YAG laser source. The pulse duration, beam size (without focusing), divergence angle, and repetition rate of the 800-nm laser were 8 ns, 4 mm, 1.3 mrad, and 10 Hz, respectively. The laser beam was focused with an $f = 20$ cm lens and passed through a 1-cm-path quartz cuvette filled with the sample solution. The position of the sample cell could be changed along the light beam direction, so that the local intensity within the sample cell could be varied to keep the laser power level constant. To avoid any self-focusing or self-defocusing effects inside the sample, the sample cell was

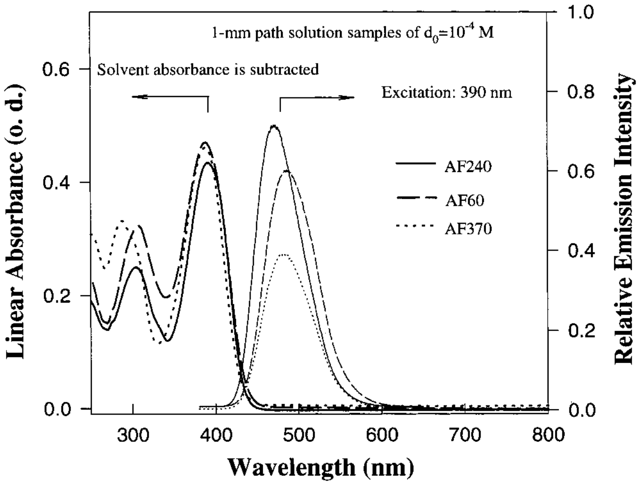

Figure 6. One-photon absorption and emission spectra of AF-60, AF-240, and AF-370 in THF at 10^{-4} M concentrations.

kept away from the focal point. The transmitted laser beam from the sample cell was detected by an optical power meter with a large detective area of 30-mm diameter. No iris was used in front of the detector. The entire transmitted laser beam was captured by the power meter, so that the influence of any possible change in the beam structure could be avoided.

To compare the effective TPA cross sections of these chromophores without interference from solvent polarity effects, the same solvent tetrahydrafuran (THF) was used for the TPA characterization of all these materials.

Effective TPA Cross Sections. The linear optical and two-photon properties for the newly synthesized dyes measured in THF solution at 800 nm are summarized in Table 1. This table includes values for β, the two-photon absorption coefficient; σ_2', the two-photon absorption cross section; and σ_2' divided by molecular weight. Before we discuss the nanosecond two-photon properties at 800 nm for the dyes containing different hetero-aromative acceptors, we emphasize that valid absolute structure/property relationships (comparisons of two-photon absorption cross sections) can only be ascertained for those molecules that have their two-photon absorption peaks at approximately the same wavelength. If the two-photon peaks are shifted in wavelength away from the experimental wavelength of 800 nm, comparisons of absolute cross sections are misleading. It is for this reason that the π-acceptor structure/property relationships deduced from the experimental data in this study are most valid at 800 nm. This wavelength was chosen because it is the optimum wavelength for imaging applications. If one wishes to compare absolute values of two-photon cross sections as a function of structure, the entire two-photon spectra of the subject molecules must be experimentally determined. Indeed, such efforts have begun to appear.[25] It should also be pointed out that the measured values represent effective cross sections measured with nanosecond pulses. These experiments are not sufficient for ascertaining the contribution of excited-state absorption to the observed effective two-photon absorption cross sections.[26] However, for preliminary screening purposes, we feel the results are adequate. In fact, for many applications that utilize the upconverted fluorescence from a nanosecond laser pulses, these values are most suitable.

Table 1. Optical Properties of Diphenylaminofluorene-Based Chromophores at 800 nm in THF

chromophore π-acceptor structure (MW)	λ_{max} (nm) linear abs. (emission, excited at 390 nm)	β (cm/GW) at 0.02 mol/L	$\sigma_{2'}$ [x 10^{-48} cm^4 s/(photon molecule)]	$\sigma_{2'}$/MW [x 10^{-50} cm^4 s mol/ (photon molecule g)]
AF50 R = decyl (717.09)	390 (492)	5.6	115.6	16.1
AF 60 R = ethyl (492.66)	388 (488)	4.7	96.9	19.7
AF-240 (552.70)	391.5 (479)	4.7	97.7	17.6
AF-370 (493.64)	386 (490)	4.1	84.5	17.1
AF-386 R = decyl (806.19)	370 (439)	3.3	67.1	8.3
AF-260 (517.67)	402.5 (552)	1.9	39.2	7.6
AF390 (506.64)	389 (468)	1.1	22.7	4.5
AF-385 R = decyl (908.32)	384 (449)	0.2	3.9	0.4

As the experimental data indicate, all of the chromophores except 2-(4,5-diphenyl)imidazolyl-end-capped **AF-385** have moderate to high nanosecond measured values for their effective two-photon absorption cross sections, σ_2'. Two of them, 2-benzothiazolyl-end-capped **AF-240** and benzoyl-containing **AF-370**, stand out as having relatively good, albeit lower, σ_2' values, as compared to that of **AF-50**, which is the most active member within the family of the diphenylamine/2-vinylpyridine-based AFX dyes. It should be pointed out that, if the contributions of the vinyl group and the alkyl-chain-length effect[27] (ethyl vs decyl) in **AF-50** (2-vinylpyridine) were to be factored out, one would argue that the 2-benzothiazolyl and benzoyl groups are better π acceptors than pyridine for the diphenylaminofluorene-based AFX chromophores, at least in the nanosecond TPA regime. Therefore, we have also included **AF-60**, which is the diethyl analogue of **AF-50**, in this effort to assess the relative π-accepting capability of the various acceptors. It is apparent that the cross sections of **AF-240** and **AF-60** are effectively the same. Furthermore, after the σ_2' values have been normalized with

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(26) Detailed deconvolution of the relative contributions of intrinsic TPA and additional absorption processes is being performed on the most promising AFX chromophores, and the results will be reported in a forthcoming paper (J. W. Baur et al.).

(27) The alkyl-chain-length effect in asymmetrical AFX chromophores will be reported in a separate paper. The synthesis and two-photon properties of the 9,9-didecyl analogue of AF-240 have been recently reported: Belfield, K. D.; Schafer, K. J.; Mourad, W.; Reinhardt, B. A. *J. Org. Chem.* **2000**, *65*, 4475.

the respective molecular weights, the σ_2'/MW values of these two species are actually slightly (5−9%) larger than that of **AF-50** (see Table 1). We attempted to correlate the σ_2' and σ_2'/MW values with the Hammett parameters (σ), inductive parameters (σ_I), and resonance parameters (σ_R) available in the literature[28] and found no obvious linear correlations. This is not surprising if we consider the fact that the TPA cross section is related to an electronic excitation process, whereas the latter parameters were experimentally determined for the pertinent molecules in their electronic ground states. Nevertheless, within the framework of our nanosecond TPA cross-section data (σ_2'/MW values), the qualitative trend for π-electron-accepting ability, i.e., ability to accept charge transferred from diphenylamine appears to be as follows: 2-(4-vinyl)pyridine > 2-benzothiazolyl > benzoyl > 2-(*N*-phenylbenzimidazolyl > 2-quinoxalinyl > 2-benzoxazolyl > 2-(4,5-diphenyl)imidazoyl.

In summary, this work suggests the 2-benzothiazolyl and benzoyl groups as two replacement candidates for 2-vinylpyridine as the π acceptor for the diphenylaminofluorene-based AFX chromophores. We have also observed that the THF solution of **AF-240** remained optically intact after repetitive exposure to nanosecond laser radiation, whereas the **AF-50** solution would darken with the passage of time when subjected to similar treatment. Thus, on the basis of its greater chemical, thermal, and photochemical stabilities, as well as its higher fluorescence efficiency (qualitatively, see Figure 6), we have chosen 2-benzothiazolyl over benzoyl in our continuing development of AFX chromophores.

Experimental Section

2,7-Dibromofluorene (**1**) and (7-bromo-9,9-didecylfluoren-2-yl)diphenylamine (**11**) were prepared as described previously.[2] 2-Iodoquinoxaline was prepared according to literature procedures[19] as follows: 2-Hydroxyquinoxaline was converted to 2-chloroquinoxaline with phosphorus oxychloride, and the resulting 2-chloro intermediate was treated with sodium iodide and hydroiodic acid (HI) in 2-butanone to afford 2-iodoquinoxaline. All other reagents and catalysts were purchased from Aldrich Chemical Co.; Lancaster Synthesis, Inc.; Strem Chemicals; or Fisher Scientific and used as received.

2,7-Dibromo-9,9-diethylfluorene (2). To a mechanically stirred mixture of 2,7-dibromofluorene (Aldrich, 66.5 g, 0.205 mol) were added powdered potassium hydroxide (56.0 g, 1.0 mol), potassium iodide (3.4 g), and dimethyl sulfoxide (DMSO, 150 mL) cooled to 10 °C; ethyl bromide (40 mL, 58.4 g, 0.536 mol) was added dropwise over 45 min. The mixture turned from red to light purple. After the temperature increased to 20 °C, the mixture was left overnight, with stir, and then poured into water to precipitate the crude product, 77.0 g (98.7% yield), mp 144−153 °C. The product was then recrystallized from hexane (550 mL) with charcoal treatment and collected in two crops, mp's 154−157 and 153−154 °C, totaling 60.36 g (77.4% yield). ^{1}H NMR (270 MHz, CDCl$_3$, ppm): 0.27, 0.30, 0.33 (triplet, CH$_3$, 6H); 1.99, 2.01, 2.04, 2.07 (quartet, CH$_2$, 4H); 7.44−7.50 (multiplets, aromatic protons, 6H). ^{13}C NMR (CDCl$_3$, noise-decoupled, ppm): 8.37, 32.83, 56.92 (sp^3 carbons); 121.27, 121.67, 126.43, 130.36, 139.61, 151.87 (sp^2 carbons).

7-Bromo-9,9-diethylfluorene-2-carboxaldehyde (4). To a mechanically stirred solution of 2,7-dibromo-9,9-diethylfluorene (**2**, 59.38 g, 0.1563 mol) in tetrahydrofuran (THF, 325 mL), cooled in a dry ice−ethanol bathwas added *n*-butyllithium (Aldrich, 104 mL of 1.6 M solution in hexanes, 0.1664 mol, 1.06 equiv) dropwise over 25 min. After 20 min, *N*,*N*-dimethylformamide (DMF, 17 mL, 0.22 mol) in THF (30 mL) was added, and the mixture was stirred in the cooling bath for 1.5 h and outside the bath for 1 h. The reaction mixture was then cooled to 5 °C and treated with aqueous HCl (12.5 mL of concentrated hydrochloric acid diluted with 50 mL water). The mixture was diluted with 200 mL of toluene, and the aqueous phase was separated and extracted with 200 mL of toluene. The combined organic phase was washed with dilute sodium bicarbonate solution, dried over magnesium sulfate, and concentrated. The residual solids were recrystallized from heptane−ethyl acetate (9:1) to give colorless solids, 40.29 g (78.4% yield), mp 126−128 °C. The mother liquor after chromatography over 150 g of silica gel, elution with 1:1 heptane−toluene, and trituration of residual solids in hexanes gave additional product, 6.56 g (12.8% yield, 91% total yield), mp 126−128 °C. MS (*m*/*z*): 328, 330 (M$^+$). A sample for elemental analysis was prepared by recrystallization from hexanes, mp 127−129 °C. Anal. Calcd. for $C_{18}H_{17}BrO$: C, 65.55%; H, 5.20%; Br 24.27%. Found: C, 65.60%; H 5.51%; Br, 24.71%. ^{1}H NMR (270 MHz, CDCl$_3$, ppm): 0.27, 0.30, 0.33 (triplet, CH$_3$, 6H); 1.99, 2.01, 2.04, 2.07; 2.10, 2.12, 2.14 (two sets of overlapping quartets, ABX$_3$, diasterotropic CH$_2$, 4H); 7.45, 7.50, 7.53, 7.63, 7.66 (complex multiplets, aromatic protons, 3H), 7.80, 7.83, 7.86, 7.87, 7.88, 7.89 (complex multiplets, aromatic protons, 3H); 10.07 (singlet, CHO proton, 1H). ^{13}C NMR (CDCl$_3$, noise-decoupled, ppm): 8.41, 32.48, 56.59 (sp^3 carbons); 120.06, 122.22, 123.11, 123.17, 126.53, 130.51, 130.60, 135.63, 138.95, 146.66, 150.29, 153.43 (sp^2 carbons); 192.05 (sp^2 carbon of CHO moiety).

2-(7-Bromo-9,9-diethylfluoren-2-yl) Benzothiazole (5). A mixture of 7-bromo-9,9-diethylfluorene-2-carboxaldehyde (**4**, 49.35 g, 0.15 mol), 2-aminothiophenol (20 mL, 0.187 mol, 1.25 equiv), and DMSO (110 mL) was heated in an oil bath to a bath temperature of 195 °C, held at that temperature for 45 min, and then poured into water. The separated solids were collected, reslurried in 1:4 acetic acid−water (1000 mL), filtered, and washed with water and dilute sodium bicarbonate solution. These solids, 80.05 g, were then reslurried in hot ethanol (600 mL), cooled, and filtered to give the benzothiazole product, 45.69 g, mp 133.6−135 °C. An additional 6.6 g, mp 134.6−135.5 °C, was obtained by chromatography of the ethanol filtrate. Total recovery 52.29 g (80.3% yield). MS (*m*/*z*): 433, 435 (M$^+$). Anal. Calcd. for $C_{24}H_{20}BrNS$: C, 66.37%; H, 4.64%; Br, 18.40%; N, 3.23%; S, 7.37%. Found: C, 66.46%; H, 4.52%; Br, 18.54%; N, 3.14%; S, 7.19%. ^{1}H NMR (270 MHz, CDCl$_3$, ppm): 0.30, 0.33, 0.36 (1:2:1, CH$_3$, 6H); 1.98, 2.01, 2.03, 2.06; 2.09, 2.12, 2.15, 2.17 (two sets of overlapping quartets, ABX$_3$, diasterotropic CH$_2$, 4H); 7.31, 7.34, 7.36; 3.37; 7.44, 7.47, 7.49; 7.50, 7.52, 7.55; 7.66, 7.69; 7.83, 7.86; 7.95, 7.96, 7.98, 7.99, 8.08, 8.11, 8.13, 8.14 (complex, aromatic protons, 10H). ^{13}C NMR (CDCl$_3$, noise-decoupled, ppm): 8.50, 32.57, 56.73 (sp^3 carbons); 120.11, 121.52, 122.10, 122.99, 125.09, 126.30, 127.28, 130.22, 132.67, 134.91, 139.44, 143.32, 150.35, 152.74, 154.12 (sp^2 carbons); 168.29 (sp^2 carbon of $-N{=}C-S-$ of thiazole moiety).

(7-Benzothiazol-2-yl-9,9-diethylfluoren-2-yl)diphenylamine (AF-240). A mixture of 2-(7-bromo-9,9-diethylfluoren-2-yl)benzothiazole (**5**, 6.6 g, 0.015 mol), potassium carbonate (10.3 g, 0.0746 mol), diphenylamine (Aldrich, 4.5 g, 0.0376 mol), potassium iodide (9.6 g 0.0173 mol), copper bronze (2.0 g, 0.0317 mol), copper(I) iodide (1.5 g, 0.0079 mol), 18-crown-6 (Adrich, 0.96 g, 0.0036 mol), and 1,2-dichlorobenzene (45 mL) was kept at 180−182 °C for 20 h, cooled, and filtered. The filtrate was concentrated, and the residue was transferred to a column of silica gel. Elution with heptane gave the product, 3.6 g (45.55% yield), mp 175−178.4 °C. Recrystallization from 9:1 heptane−toluene raised the mp to 178−180 °C. MS (*m*/*z*): 522 (M$^+$). Anal. Calcd. for $C_{36}H_{30}N_2S$: C, 82.76%; H, 5.79%; N, 5.36%; S, 6.12%. Found: C, 82.41%; H, 5.52%; N, 5.25%; S, 5.99%. ^{1}H NMR (270 MHz, CDCl$_3$, ppm): 0.36, 0.39, 0.41 (1:2:1, CH$_3$, 6H); 1.88 1.91, 1.93, 1.96; 2.04, 2.07, 2.09, 2.12 (two sets of quartets, ABX$_3$, diasterotropic CH$_2$, 4H); 6.98−7.35 (complex, aromatic protons, 14H); 7.42, 7.43 (1H); 7.46, 7,48, 7.49 (1H); 7.56, 7.59 (doublet, 1H); 7.64, 7.67 (doublet, 1H);

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7.83, 7.86 (doublet, 1H); 7.962, 7.967, 7.992, 7.997 (1H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.58, 32.57, 56.36 (sp^3 carbons); 118.73, 119.34, 121.01, 121.38, 121.50, 122.79, 123.22, 124.11, 124.89, 126.22, 127.28, 129.24, 131.43, 134.89, 135.29, 144.45, 147.79, 148.07, 150.67, 152.08, 154.21 (sp^2 carbons); 168.75 (sp^2 carbon of $-N{=}C-S-$ of thiazole moiety).

(7-Bromo-9,9-diethylfluoren-2-yl)diphenylamine (3). *9,9-Diethylfluorene (**7**).*[16] To a mechanically stirred mixture of fluorene (83.2 g, 0.5 mol) were added powdered potassium hydroxide (140 g, 2.5 mol), potassium iodide (4.0 g, 0.024 mol), and DMSO (225 mL) cooled to 15−20 °C; bromoethane (104 mL, 151.84 g, 1.39 mol) was added over a period of 1.5 h, and the mixture was stirred at room temperature overnight. The mixture was diluted with water (1200 mL) and extracted with toluene (2 × 400 mL). The toluene extract was washed with water, dried, and concentrated to give 116.66 g of a red oil. This oil was distilled at 1.2 mm, bp 125 °C, to afford 9,9-diethylfluorene as a colorless oil that solidified, 104.32 g (94% yield), mp 29−30 °C. MS (*m*/*z*): 222 (M^+).

*2-Bromo-9,9-diethylfluorene (**8**).* To a solution of 9,9-diethylfluorene (**7**, 22.1 g, 0.1 mol) in propylene carbonate (100 mL) was added *N*-bromosuccinimide (Aldrich, 17.8 g, 0.1 mol) at 57 °C in one portion, and the mixture was stirred for 30 min at 60 °C. The mixture was diluted with 1200 mL of water and extracted into 500 mL of toluene. The toluene extract was washed with 300-mL portions of water, dried, and concentrated. The crude product from three batches of the same size totaled 117 g of oil. This oil was distilled at 2 mm. The first fraction, bp 90−93 °C, 22.33 g, was found to be propylene carbonate. The second fraction, bp 155−165 °C, 81.0 g (89.7% yield), which solidified on cooling, mp 48.2−50.2 °C, was the desired monobromo diethyl fluorene. Recrystallization from 2-propanol−water raised the mp to 51.4−53.1 °C. MS (*m*/*z*): 300, 302 (M^+). Anal. Calcd. for $C_{17}H_{17}Br$: C, 67.79%; H, 5.69%; Br, 26.53%. Found: C, 68.32%; H, 6.04%; Br, 26.73%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.27, 0.30, 0.33 (triplet, CH_3, 6H); 1.94, 1.97, 2.00, 2.02 (quartets, CH_2, 4H); 7.20−7.78 (complex, fluorene aromatic protons, 7H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.41, 32.63, 56.36 (sp^3 carbons); 119.68, 120.95, 122.85, 126.16, 126.97, 127.43, 129.90, 140.36, 140.50, 149.40, 152.11 (sp^2 carbons).

*2-Bromo-9,9-diethyl-7-iodofluorene (**9**).* A mixture of 2-bromo-9,9-diethylfluorene (**8**, 81.0 g, 0.263 mol), acetic acid (450 mL), water (47 mL), concentrated sulfuric acid (14 mL), iodine (26.8 g, 0.106 mol), iodic acid (10.5 g, 0.06 mol), and carbon tetrachloride (21 mL) was maintained at 80−85 °C for 2.5 h with mechanical stirring The product slurry was cooled to room temperature and filtered, and the solids were washed with 1:1 acetic acid−water and water. The air-dried solids weighed 122 g, mp 162−164 °C. These solids were reslurried in 500 mL of hot methanol for 30 min and filtered, 96.94 g (86.3% yield), mp 165.3−166.6°. MS (*m*/*z*): 474 (M^+, diiodo), 426, 428 (M^+, desired bromoiodo). This material was used without further purification in the next step. A diiodo-free sample was obtained by two successive recrystallizations of a small amount of the crude product from hexanes, mp 167−168 °C. Anal. Calcd. for $C_{17}H_{16}BrI$: C, 47.80%; H, 3.78%; Br, 18.71%; I, 29.71%. Found: C, 47.64%; H, 3.78%; Br, 18.59%; I, 30.19%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.28, 0.31, 0.33 (triplet, CH_3, 6H); 1.93, 1.96, 1.99, 2.02 (quartet, CH_2, 4H); 7.39; 7.42, 7.43, 7.44; 7.46; 7.50; 7.54; 7.64, 7.65, 7.66 (complex, aromatic protons, 6H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.41, 32.54, 56.62 (sp^3 carbons); 92.96, 121.10, 121.38, 121.61, 126.16, 130.16, 132.12, 136.07, 139.49, 140.04, 151.50, 151.85 (sp^2 carbons).

(7-Bromo-9,9-diethylfluoren-2-yl)diphenylamine (3). A mixture of 2-bromo-9,9-diethyl-7-iodofluorene (**9**, 42.7 g, ca. 0.1 mol), potassium carbonate (60.0 g, 0.435 mol), copper bronze (3.3 g, 0.052 mol), 18-crown-6 (2.0 g, 0.0076 mol), diphenylamine (2 0.9 g, 0.1235 mol), and 1,2-dichlorobenzene (140 mL) was kept at reflux for 5.5 h, cooled, and filtered. The residue after concentration of the filtrate was transferred to a column of 525 g of silica gel. Elution with hexanes removed the dichlorobenzene and unreacted bromoiodofluorene (3.16 g, 7.4%). Elution with 9:1 hexane−toluene gave the product, collected after trituration with methanol, 31.24 g (67% yield), mp 154−156.5 °C. MS (*m*/*z*): 515 (M^+, iododiphenylaminofluorene), 467, 469 (M^+, desired product). The sample containing small quantities of the iodo derivative was used in subsequent reactions. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.32, 0.35, 0.38 (triplet, CH_3); 1.82, 1.84, 1.86, 1.87, 1.88, 1.89, 1.91 (complex multiplets, CH_2); 6.97−7.60 (complex multiplets, aromatic protons). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.49, 32.54, 56.32 (sp^3 carbons); 119.08, 120.11, 120.34, 120.43, 122.62, 123.54, 123.92, 126.05, 129.18, 129.96, 147.59, 147.90, 150.90, 152.11, 152.31 (sp^2 carbons).

(7-Quinoxalin-2-yl-9,9-diethylfluoren-2-yl)diphenylamine (AF-260). To a solution of (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (**3**, 9.4 g, 20 mmol) in THF (100 mL) cooled to −50 °C was added *n*-butyllithium (15 mL of a 1.6 M solution in hexanes, 24 mmol) under nitrogen atmosphere. After 45 min, a solution of tributyltin chloride (Aldrich, 6.5 mL, 24 mmol) in THF (15 mL) was added, and the reaction mixture was stirred in the bath for 45 min. Over a 1.5-h period, the reaction temperature was allowed to rise to 20 °C. After the mixture was cooled in an ice bath, a solution of potassium fluoride in water was added. The resulting mixture was stirred for 1 h and then diluted with 1:1 heptane−toluene (200 mL). The organic phase was dried and concentrated to afford 7-(1,1-dibutyl-1-stannapentyl)-9,9-diethylfluoren-2-yl)diphenylamine as an oil, 18 g. This oil was dissolved in toluene (100 mL) and treated with 2-iodoquinoxaline[19] (5.0 g, 19.5 mmol), and the mixture was degassed by bubbling nitrogen. To the degassed solution was added *trans*-dichloro(bistriphenylphosphine)palladium(II) (Strem Chemical, 750 mg, 1.07 mmol), and the mixture was kept at 95 °C for 18 h. After the mixture was cooled, a solution of potassium fluoride was added, and the insoluble fluoride was filtered off. The filtrate was dried and concentrated, and the residue was transferred to a column of alumina (250 g). Elution with 1:1 toluene−heptane, followed by recrystallization from the same solvent mixture, gave the product, 4.41 g, mp 213-215 °C (42.6% yield). Further recrystallizations did not increase the mp 213-214.5 °C. MS (*m*/*z*): 517 (M^+). Anal. Calcd. for $C_{37}H_{31}N_3$: C, 85.85%; H, 6.04%; N, 8.12%. Found: C, 85.77%; H, 5.97%; N, 7.89%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.39, 0.42, 0.45 (1:2:1, CH_3, 6H); 1.92, 1.95, 1.97, 2.00; 2.06, 2.09, 2.11, 2.14 (two sets of quartets, ABX_3, diasterotropic CH_2, 4H); 6.99−7.30 (complex, 13H); 7.62−7.78 (complex, 4H), 8.09−8.19 (complex, 3H); 9.39 (singlet, proton in the nitrogen-containing ring of quinoxaline, 1H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.82, 32.63, 56.33 (sp^3 carbons); 118.93, 119.56, 120.98, 121.70, 122.73, 123.34, 124.06, 126.71, 129.21, 129.47, 130.13, 134.60, 135.46, 141.37, 142.34, 143.61, 147.84, 147.96, 150.87, 152.02, 152.11 (sp^2 carbons).

(7-Benzoxazol-2-yl-9,9-diethylfluoren-2-yl)diphenylamine (AF-390). A mixture of cesium carbonate (6 5 g, 20 mmol; previously dried at 190 °C under 1 mmHg for 1 h), (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (**3**, 7.4 g, 16.0 mmol), benzoxazole (Aldrich, 2.4 g, 20 mmol), copper(I) iodide (0.38 g, 2.0 mmol), palladium(II) acetate (Strem Chemical, 0.075 g, 0.334 mmol), triphenylphosphine (Strem Chemical, 0.15 g, 0.6 mmol), and DMF (30 mL) was kept at 115 °C for 18 h under an atmosphere of nitrogen, cooled, diluted with toluene, and filtered. The filtrate was washed with water, dried, and concentrated. The residue was chromatographed over alumina. Earlier fractions gave 0.25 g, mp 102−104 °C, identified as 2-phenylbenzoxazole by mass spectroscopy (*m*/*z* 195). Elution with heptane−toluene (3:1) followed by crystallization gave 5.14 g (65% yield) of bright yellow crystals, mp 193−194 °C. A sample for analysis was obtained by sublimation under a 0.5-mmHg vacuum at a bath temperature of 210 °C. MS (*m*/*z*): 506 (M^+). Anal. Calcd for $C_{36}H_{30}N_2O$: C, 85.34%; H, 5.97%; N 5.53%. Found: C, 85.25%; H, 5.97%; N 5.55%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.36, 0.39, 0.41 (triplet, CH_3, 6H); 1.97, 1.95, 1.92, 1.90; 2.12, 2.10, 2.08, 2.05 (two sets of quartets, ABX_3, diasterotropic CH_2, 4H); 6.99−7.36 (complex, 14H), 7.55−7.62 (complex, 2H) 7.01−7.79 (complex, 2H), 8.20−8.24 (complex, 2H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.55, 32.60, 56.36 (sp^3 carbons); 110.41, 118.64, 119.34, 119.71, 121.15, 121.87, 122.88, 123.22, 124.20, 124.60, 124.81, 127.00, 129.27, 135.17, 142.26, 144.96, 147.78, 148.28, 150.5, 150.70, 152.16, 163.85 (sp^2 carbons).

7-(Diphenylamino)-9,9-diethylfluoren-2-yl Phenyl Ketone (AF-370). To a solution of (7-bromo-9,9-diethylfluoren-2yl)diphenylamine (**3**, 11.75 g, 0.025 mol) in THF (110 mL) cooled in a dry ice−acetone bath was syringed a 1.6 M solution of *n*-butyllithium in hexanes (21 mL, 0.0336 mol, 1.344 equiv) to give a pale yellow solution. After 45 min, a solution of benzonitrile (4 mL, 0.04 mol) in THF (10 mL) was added dropwise, at which point the reaction mixture acquired a dark red color. After 1.5 h, the reaction temperature was allowed to rise to 0 °C. The reaction was treated with water (30 mL) and concentrated hydrochloric acid (45 mL) to give a suspension of orange solids. The mixture was kept at reflux for 8 h to give a two-phase solution with no suspended solids. After being cooled, the mixture was treated with dilute aqueous sodium hydroxide and extracted into toluene. The toluene extract was washed with water, dried, and concentrated. The residual solids were chromatographed over silica gel, the column was eluted with 1:1 toluene−heptane to give the product, and the product was recrystallized from 2:1 heptane−toluene, 10.63 g (86% yield), mp 184.9−186.5 °C. Two additional recrystallizations did not increase the mp, 185−186 °C. MS (*m*/*z*): 493 (M$^+$). Anal. Calcd. for $C_{36}H_{31}NO$: C, 87.59%; H, 6.33%; N, 2.84%. Found: C, 87.28%; H, 6.62%; N, 2.57%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.36, 0.38, 0.41 (triplet, CH_3, 6H); 1.84, 1.87, 1.90, 1.93, 1.96 1.99, 2.02, 2.04 (two sets of overlapping quartets, ABX_3, diasterotropic CH_2, 4H); 7.00−7.29 (complex); 7.45−7.67 (complex); 7.76−7.83 (complex, aromatic protons, 21H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 8.55, 32.43, 56.21 (sp^3 carbons); 118.44, 121.38, 122.96, 124.26, 128.18, 129.27, 129.88, 130.39, 131.98, 134.80, 135.03, 138.46, 145.92, 147.73, 148.48, 149.83, 152.60 (sp^2 carbons); 196.68 (carbonyl carbon).

7-(Diphenylamino)-9,9-didecylfluorene-2-carboxaldehyde (12). To a solution of (7-bromo-9,9-didecylfluoren-2-yl)-diphenylamine[2] (**11**, 34.6 g, 0.05 mol) in THF (200 mL) cooled to less than −50 °C was added a solution of *n*-butyllithium in hexanes (1.6M, 45 mL, 0.072 mol) over 15 min. After 30 min, a solution of DMF (7.5 mL, 0.097mol) in THF (40 mL) was added, and after 1 h, the temperature was allowed to rise to 0 °C. The mixture was cooled in an ice bath and treated with dilute hydrochloric acid (7.5 mL of concentrated HCl mixed with 60 mL of water). After dilution with toluene (200 mL), the organic phase was washed with water, aqueous sodium bicarbonate, and saturated sodium chloride solution; dried; and concentrated. The residue was chromatographed over 500 g of silica gel. After elution with 20% toluene−heptane and removal of solvent, the product, which was initially obtained as a glassy solid, crystallized into yellow solids on standing with methanol (150 mL), 28.2 g (88% yield), mp 77−78.5 °C. Anal. Calcd. for $C_{46}H_{59}NO$: C, 86.06%; H, 9.26%; N, 2.18%. Found: C, 85.81%; H, 9.49%; N, 2.10%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.61−0.65 (broad); 0.83, 0.85, 0.88 (triplet); 1.05−1.29 (complex, broad); 1.80−2.00 (complex multiplet, decyl protons, 20H); 7.02, 7.03, 7.04, 7.05, 7.06, 7.07, 7.12,, 7.15, 7.24, 7.26, 7.29, 7.59, 7.62, 7.69, 7.72, 7.80, 7.82, 7.83 (complex multiplets, aromatic protons, 16H); 10.02 (singlet, CHO proton, 1H). ^{13}C NMR ($CDCl_3$, noise-decoupled, ppm): 14.11, 22.66, 23.84, 29.11, 29.29, 29.55, 29.92, 31.88, 40.03, 55.15 (sp^3 carbons); 118.21, 119.11, 121.70, 122.82, 123.11, 123.31, 124.38, 129.30, 130.83, 134.02, 134.51, 147.49, 147.64, 148.85, 151.30, 153.69 (sp^2 carbons); 192.19 (sp^2 carbon of CHO moiety).

(7-(4,5-Diphenylimidazol-2-yl)-9,9-didecylfluoren-2-yl)-diphenylamine (AF-385). A mixture of 7-(diphenylamino)-9,9-didecylfluorene-2-carboxaldehyde (**12**, 4.18 g, 6.5 mmol), benzil (Aldrich, 1.6 g, 7.6 mmol), ammonium acetate (4.5 g), and acetic acid (30 mL) was heated under nitrogen in an oil bath to a bath temperature of 123 °C, held at that temperature for 2 h, cooled, and filtered. The solid product was washed with 50 mL of 1:1 acetic acid−water, washed with water, and dried, 5.2 g (93% yield), mp 228.4 232.4 °C. The sample was digested in a mixture of ethyl acetate (20 mL) and hexanes (100 mL), and the resulting mixture was filtered to remove a small quantity of benzil. The product was then recrystallized two times from toluene and two times from toluene−ethanol (2:1), mp 236.7−238.7 °C. MS (*m*/*z*): 831 (M$^+$). A sample for analysis was dried at 180 °C at 0.2 mmHg for 5 h. Anal. Calcd. for $C_{60}H_{69}N_3$: C, 86.59%; H, 8.36%; N 5.05%. Found: C, 86.43%; H, 8.40%; N, 4.92%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.64−0.66 (broad); 0.80, 0.83, 0.85 (triplet); 1.04−1.11 (complex, broad); 1.76−1.26 (complex, broad); 1.89−1.93 (complex multiplet, decyl protons, 20H); 6.97, 6.98, 6.99, 7.00, 7.01, 7.02, 7.06, 7.08, 7.09, 7.21, 7.24, 7.27, 7.30, 7.31, 7.33, 7.34, 7.36, 7.37, 7.40, 7.52, 7.60, 7.64, 7.69, 7.91, 8.09, 8.11 (complex multiplets, aromatic protons, 26H); 12.45 (singlet, NH proton, 1H). The solubility of this compound is too low for ^{13}C NMR experiment.

(9,9-Didecyl-7-(1-phenylbenzimidazol-2-yl)fluorenyl-2-yl)diphenylamine (AF-386). A mixture of 7-(diphenylamino)-9,9-didecylfluorene-2-carbaldehyde (**12**, 3.21 g, 5 mmol), *N*-phenyl-l,2-phenylenediamine (Aldrich, 1.0 g, 5.42 mmol), and ethanol (35 mL) was kept under reflux for 2 h. TLC revealed very little reaction and the presence of both starting materials. The reaction mixture was cooled and treated with copper(II) acetate (2.0 g, 10 mmol) and then kept under reflux for 15 min. After evaporation of methanol, the residue was extracted into 1:1 toluene−heptane, and the extract was passed through a column of alumina to recover the unreacted starting aldehyde. Continued elution with 3:1 toluene−heptane gave a small quantity of product, which was allowed to stand with methanol in the refrigerator. Almost colorless solids were then collected, 0.47 g (12% yield), mp 101.5−102.8 °C. MS (*m*/*z*): 805 (M$^+$). Anal. Calcd. for $C_{58}H_{67}N_3$: C, 86.41%; H, 8.38%; N 5.21%. Found: C, 86.22%; H, 8.43%; N, 5.14%. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 0.46−0.52 (broad); 0.82, 0.85, 0.87 (triplet); 0.90−1.27 (complex, broad); 1.58−1.70 (complex multiplet, decyl protons, 20H); 6.98, 7.00, 7.02, 7.06, 7.07, 7.09, 7.11, 7.20, 7.23, 7.24, 7.25, 7.26, 7,28, 7.30, 7.32, 7.33, 7.34, 7.35, 7.43, 7.45, 7,47, 7.48, 7.50, 7.51, 7.52, 7.55, 7.58, 7.61, 7.75, 7.78, 7.90, 7.93 (complex multiplets, aromatic protons, 25H). ^{13}C NMR (noise-decoupled, $CDCl_3$, ppm): 14.11, 22.63, 23.73, 29.26, 29.40, 29.55, 29.63, 29.97, 31.88, 40.14, 54.97 (sp^3 carbons); 110.26, 118.90, 119.11, 119.68, 120.83, 122.62, 122.94, 123.17, 123.34, 123.63, 123.91, 127.49, 128.32, 128.81, 129.16, 129.73, 135.23, 137.16, 137.33, 142.23, 143.04, 147.70, 147.84, 150.18, 152.57 (sp^2 carbons); 153.20 (carbon in the −N═C−N− unit of benzimidazole moiety).

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