

Highly Active Two-Photon Dyes: Design, Synthesis, and Characterization toward Application

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Received January 21, 1998. Revised Manuscript Received May 18, 1998

A series of compounds with systematically varied molecular structures which exhibit very large effective two-photon cross sections has been synthesized and characterized in solution using a nonlinear transmission technique. The general structure of these compounds can be categorized into two basic structural families: acceptor/donor/donor/acceptor and donor/bridge/acceptor. This study attempts to determine certain molecular structure/effective two-photon absorption relationships by careful characterization and as a function of systematically varied changes in the organic structure of the dye molecules. Such information can be useful in the design of more efficient two-photon dyes for imaging and power-limiting applications. The results of the study indicate that with the incorporation of certain combinations of structural elements, dyes can be synthesized which have greatly increased effective cross sections as high as $152.5 \times 10^{-48} \text{ cm}^4 \text{ s/photon molecule}$ in benzene solution at 800 nm using 8 ns pulses. This value is orders of magnitude higher than commercially available organic dyes measured at the same wavelength. Although the process is thought to involve a combination of two-photon absorption and excited state absorption phenomena, the information gathered from these new families of dyes has provided an important first step in producing improved materials for use in many different two-photon technology application.

Introduction

The two-photon process, predicted theoretically in 1931¹ and observed experimentally in the 1960s,² has received little consideration for practical application. The lack of availability of dyes with sufficiently large cross sections has made many practical applications appear unattainable. More recently, the synthesis of new dyes³ with increased cross sections and large upconverted fluorescence has opened up a myriad of new applications. These new applications include two-photon upconverted lasing,⁴ two-photon optical power limiting,⁵ three-dimensional optical data storage, and

photodynamic therapy.⁶ Another application which has, unlike the others, received a reasonable amount of attention is three-dimensional imaging using two-photon laser scanning confocal microscopy.⁷ Multiphoton microscopy appears to be of great value as an imaging technique for numerous biological systems⁸ as well as organic paints and coatings.⁹ This technique like the others has never reached its full potential due to the lack of dyes which exhibit high intensity upconverted fluorescence. A tremendous improvement in the

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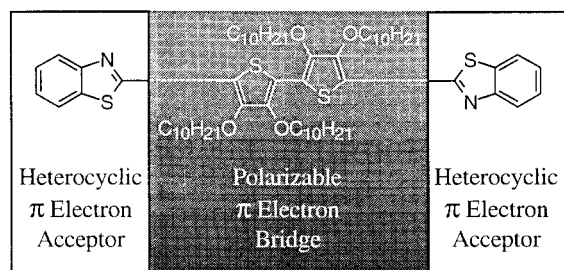


Figure 1. Type I chromophores.

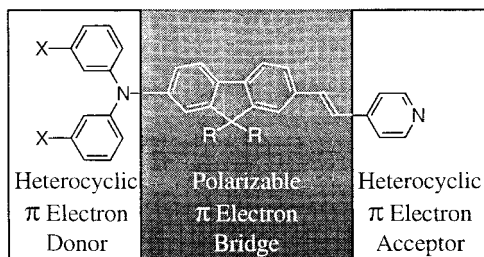


Figure 2. Type II chromophores.

depth of confocal microscopic imaging can be obtained when the two-photon peak occurs at or near 800 nm, a wavelength at which most organic and biological materials have large optical transparency. The Air Force currently has a strong interest in the development of two-photon technology as both an imaging tool for the nondestructive evaluation (NDE) of aircraft paint and also as a useful material for optical power limiting. It became evident that in order for two-photon technology to realize its full potential, major improvements would be necessary in the design and synthesis of more active dye molecules with the necessary solubility and photostability. To facilitate the design and synthesis of new more active molecules, research was needed to establish well-defined structure/property relationships for a large number of organic structures. This requires both the synthesis of highly pure, well-defined organic dyes with systematically varied molecular structures and the careful reproducible characterization of their two-photon properties. This report describes the design, synthesis, and characterization of two new families of two-photon dyes specifically designed for use at 800 nm and carried out in our combined laboratories over the past 3 years. Other research groups have investigated the design of organic two-photon materials based on bis-donor-containing stilbene molecules which exhibit the maxima of their two-photon absorptions at shorter wavelengths.¹⁰

The interpretation of the experimental data in an attempt to define some two-photon property/molecular structure relationships will also be presented.

Molecular Design

The design of the chromophores was, in this initial study, focused on two general organic structural types. Type I chromophores (Figure 1) are symmetrical in nature, consisting of a π electron rich thiophene aromatic bridge flanked on either side with an electron poor heterocyclic benzothiazole group. Type II chromophores (Figure 2) are asymmetrical molecules consisting of a highly fluorescent π electron rich aromatic/olefinic

bridge flanked on one side by a thiophene or diarylamine π electron donor and on the other by a pyridine heterocyclic π electron acceptor. Pendant alkyl chains (R) are added to the aromatic bridge for solubility and π electron donor functional groups (X) can be added to the aryl groups on the amine to increase electron density or provide reactive functional groups for the formation of high molecular weight polymers.

The initial molecular design concept was focused on using the effective molecular two-photon absorption cross section that is related to the imaginary part of the third-order nonlinear susceptibility of the medium at the two-photon absorption frequency. Structural elements which increase the effective conjugation length and polarizability of the molecule should increase the two-photon absorption cross section. The major molecular design challenge was to increase the molecular two-photon cross section without shifting the two-photon absorption peak away from 800 nm.

Synthesis

The type I chromophores, compounds **1** and **2**, were synthesized according to the schemes described in Figure 3 in yields of 53 and 25%, respectively. The asymmetrical type II chromophores were synthesized by a number of different routes. The syntheses of type II chromophores which incorporated fluorene or biphenyl aromatic π electron bridges and which were synthesized via bromo diphenylamino intermediates are depicted in Figure 4. The palladium-catalyzed monosubstitution of an aromatic bromo group on an appropriately substituted fluorene with the lithium salt of diphenylamine afforded the bromo amino fluorenes **7–10** in yields ranging from 20 to 35%. The palladium-catalyzed substitution of the remaining bromo group under Heck reaction conditions produced the chromophores **11–15** in yields of 45 to 60%. The purified dyes are highly soluble in organic solvents and are fluorescent greenish yellow in the solid state. The dyes were highly purified using column chromatography which in some cases was followed by recrystallization from an appropriate organic solvent. In other cases the dyes were isolated as purified oils which were allowed to stand for several days before crystallization would take place. In most of the cases, the purified dyes needed to have all traces of solvent removed before crystallization would take place. The synthesis of dyes which contained substituted diphenylamino electron-donating groups coupled with fluorene bridges followed a slightly different scheme involving two different routes (Figure 5). The initial route involved a palladium-catalyzed coupling of a lithium salt of a dimethoxydiphenylamine to a vinylpyridyl-substituted fluorene to form the dimethoxy-substituted analogue of compound **11** designated as compound **17**. It was discovered that although this route did produce compound **17** in a manageable overall yield, the deprotection to form the dihydroxy compound was not straightforward and produced many byproducts. The alternate route to first form compound **18** followed by deprotection to form the dihydroxy diarylamine and finally followed by a Heck reaction to form the desired dihydroxy dye proved much more facile.

(10) Ehrlich, J. E.; Wu, X. L.; Lee, I.-Y. S.; Hu, Z.-Y.; Rockel, H.; Marder, S. R.; and Perry, J. W., *Optics Lett.* **1997**, *22* (24), 1843.

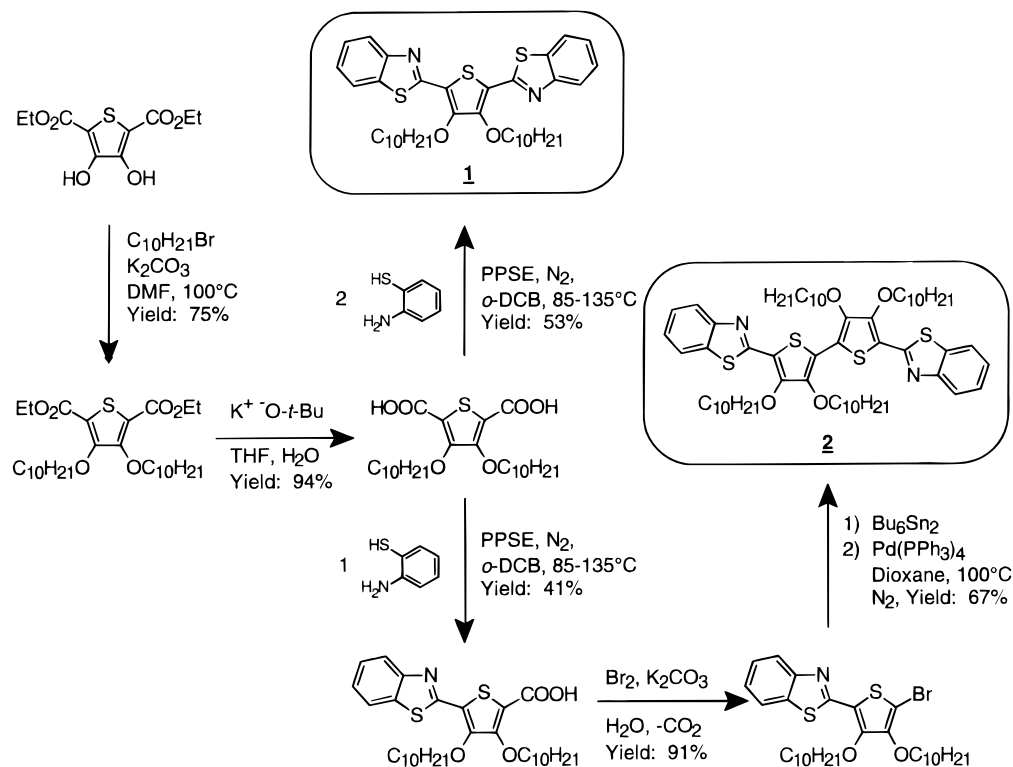


Figure 3. Synthetic scheme for type I chromophores **1** and **2**.

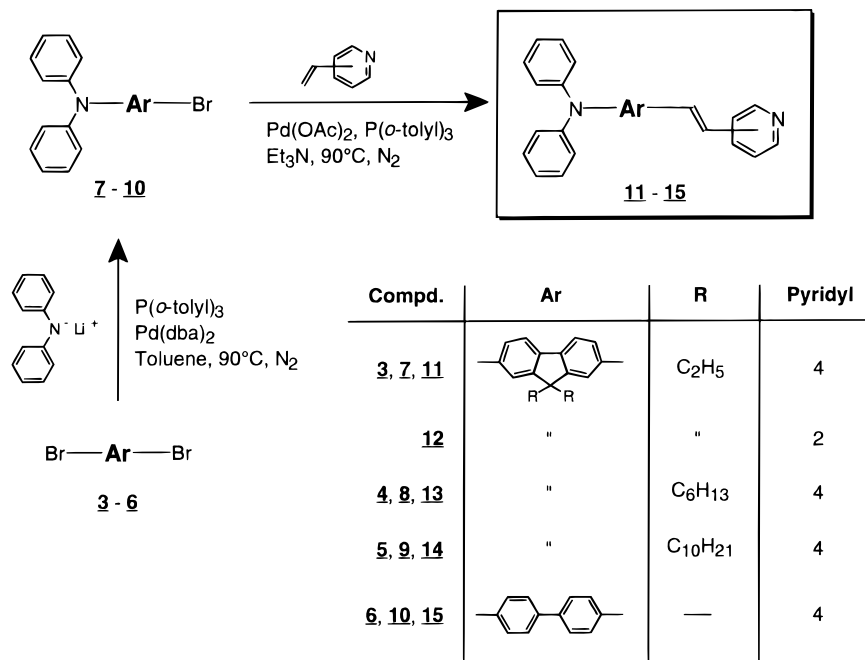


Figure 4. Synthetic scheme for compounds **11**–**15**.

Another type II dye with a fluorene bridging group which was investigated contained a pyridine acceptor coupled with a heterocyclic ring π electron donor, thiophene. This compound was synthesized via the scheme in Figure 6 by the palladium-catalyzed Stille coupling of 4-(tri-*n*-butylstannyl)pyridine with 2,7-dibromo-9,9-di-*n*-decyl-9*H*-fluorene to produce compound **21**. Compound **21** was then reacted in an analogous manner with 2-(tri-*n*-butylstannyl)thiophene to form the donor-acceptor dye **22**.

A third example of a type II dye was designed to have increased conjugation length via the incorporation of a

second fluorene group in the π electron bridging unit. Compound **7** was converted to the tri-*n*-butyltin derivative **23** in high yield. The reaction of the tin compound **23** with the vinylpyridyl derivative **16** under palladium-catalyzed Stille coupling conditions gave the bifluorene-containing compound **24** in 49% yield (Figure 7).

A final bridging group which was investigated was 2,6-naphthyl. This bridging group was chosen for its high degree of planarity, its strong fluorescence emission, and its presence in highly active second-order nonlinear optical materials.¹¹ The reaction of the commercially available 2-bromo-6-hydroxy-naphthalene **25**

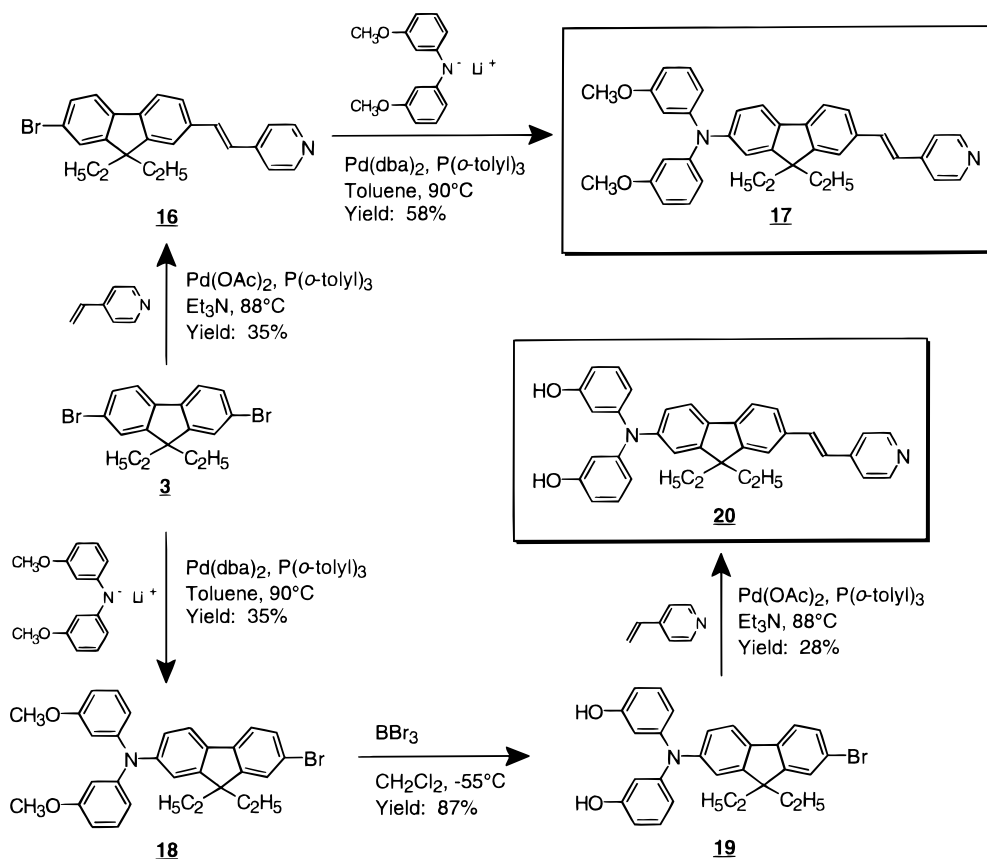


Figure 5. Synthetic scheme for compounds 17 and 20.

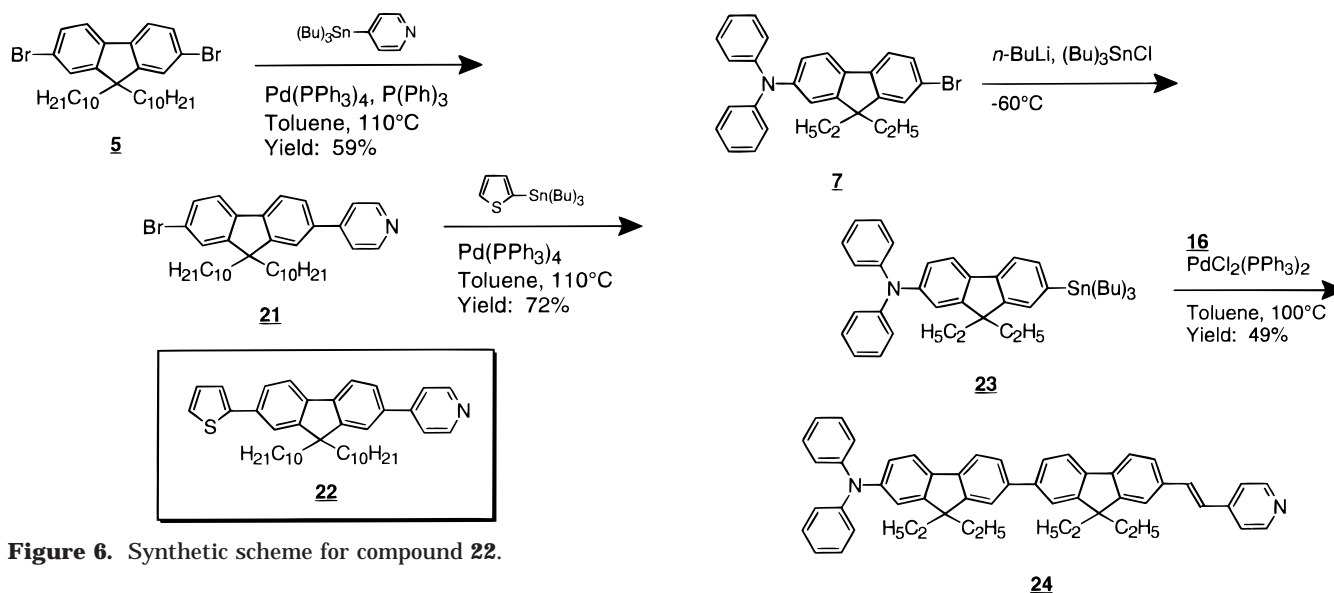


Figure 6. Synthetic scheme for compound 22.

with aniline gave the naphthylamine **26** in 88% yield. Compound **26** then served as an intermediate for two syntheses. The reaction of compound **26** with 4-(tri-*n*-butylstannyl)pyridine gave the Stille coupling product **27** in 42% yield. The copper-catalyzed reaction of **27** with iodobenzene in *o*-dichlorobenzene at 180°C gave the diphenylamino pyridylnaphthalene **28** in 86% yield. If **26** is reacted first with iodobenzene as described above, the diphenylamino bromonaphthalene **29** is isolated in 77% yield. Compound **29** was then reacted

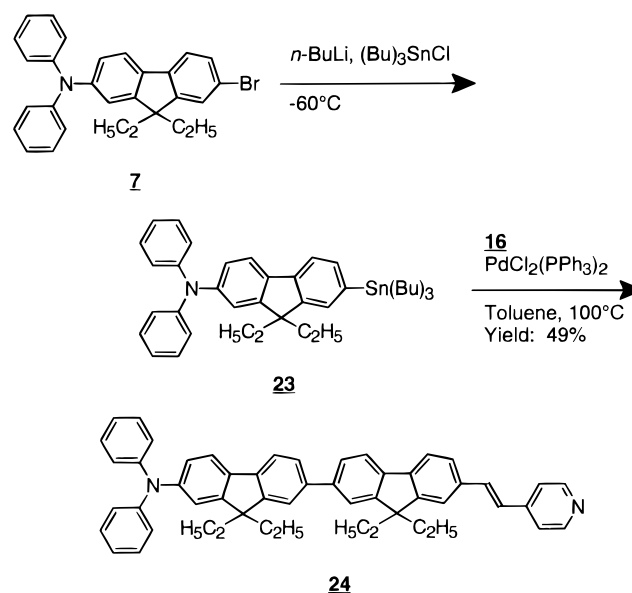


Figure 7. Synthetic scheme for compound 24.

with 4-vinylpyridine under Heck conditions to give the 4-vinylpyridyl dye **30** in 42% yield. This series of reactions is shown in Figure 8.

Solution Characterization of Two-Photon Properties

These two series of organic two-photon materials have strong linear absorption around 400 nm, but no absorption in the spectra ranging from 500 to 850 nm. So upon irradiation with a laser at 800 nm, there should be no

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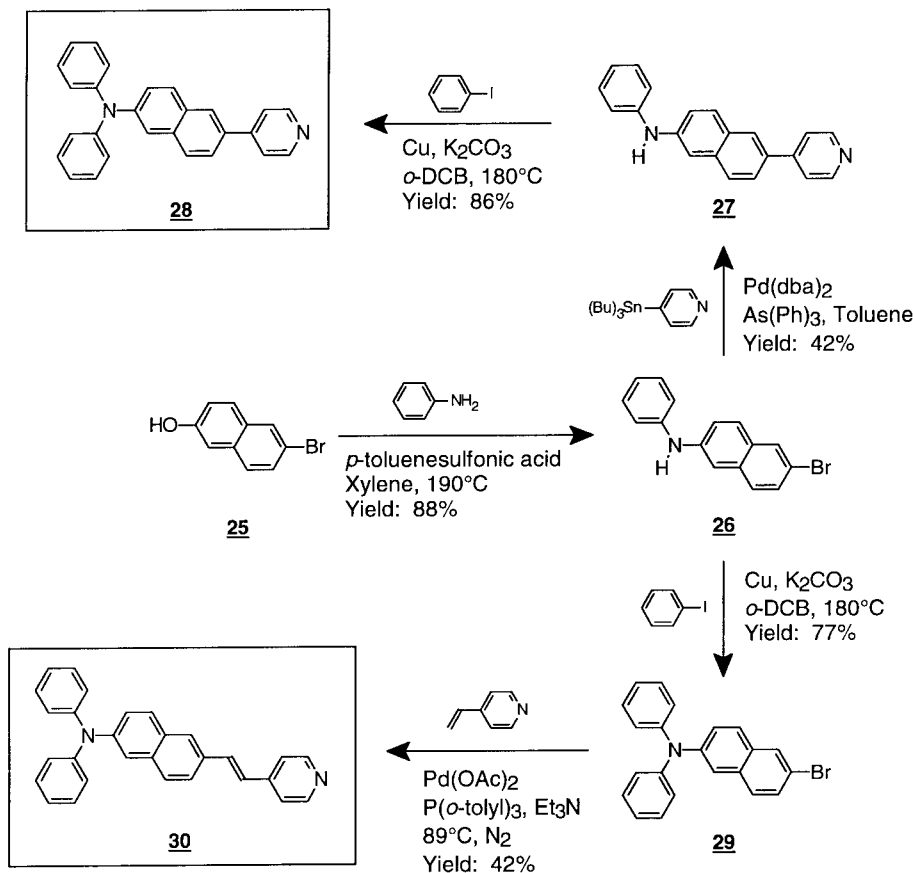


Figure 8. Synthetic scheme for compounds **28** and **30**.

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 type II dye solutions excited even with an unfocused Q-switched near-IR laser beam at the wavelength mentioned above. This indicates that a quite strong two-photon absorption process is occurring within the samples. Several methods can be used to investigate the two-photon resonance and determine the two-photon absorption cross section. They are (a) nonlinear transmission, (b) upconverted fluorescence emission, (c) transient absorption, and (d) four-wave mixing. The nonlinear transmission technique, which was adopted for use in this study, is direct and very convenient. However, one thing should be kept in mind when using the transmission method: the concentration of dye should not be too high in order to avoid the formation of aggregates of solute in the solution. The presence of aggregates larger than the wavelength of the incident light will result in scattering and reduce the precision of this measurement. This technique involves the measurement of the transmitted intensity as a function of the incident intensity. The relationship will be linear if there is no nonlinear absorption. If the nonlinear transmission change is only due to the TPA (two-photon absorption) process, the transmitted intensity I can be expressed as

$$I = \frac{I_0}{1 + I_0 L \beta} \quad (1)$$

where I_0 is the incident intensity, L is the thickness of

the given sample, and β is the TPA coefficient of the given material. In the derivation of eq 1 it is assumed that the incident beam has a uniform transverse intensity distribution. It is also assumed that the beam is focused near the sample and that there is a Gaussian transverse intensity distribution in the molecular medium, and eq 1 should be modified as¹²

$$I = \frac{I_0 \ln(1 + I_0 L \beta)}{I_0 L \beta} = \frac{\ln(1 + I_0 L \beta)}{L \beta} \quad (2)$$

The nonlinear absorption coefficient β should be independent of the input intensity I_0 for any given sample. However, if there are other additional nonlinear absorption mechanisms such as excited-state absorption, three-photon absorption, or considerable beam-profile changes within the sample due to self-focusing or defocusing, the measured nonlinear absorption coefficient β value will not appear to remain constant. We have already confirmed that the measured β values are basically the same within the experimental uncertainty;¹⁰ therefore, in our case the major contribution to the observed nonlinear absorption should be due to a TPA process. If the nonlinear absorption coefficient β is experimentally measured we can determine the molecular two-photon cross section σ_2 using the following expression⁵

(12) He, G. S.; Yuan, L.; Cheng, N.; Bhawalkar, J. D.; Prasad, P. N.; Brott, L. L.; Clarkson, S. J.; Reinhardt, B. A. *J. Opt. Soc. Am. B* **1997**, *14* (5), 1079.

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \quad (3)$$

Here β is in units of cm/GW, N_0 is the molecular density of the TPA compound (in units of cm⁻³), σ_2 is in units of cm⁴/GW, d is the concentration of the TPA compound in units of mol/L, and N_A is the Avogadro constant.

In some reference papers, the molecular TPA cross section is expressed in a form not containing energy units,

$$\sigma_2' = h\nu\sigma_2 \quad (4)$$

where $h\nu$ is the energy of the incident photon, and σ_2' is in units of cm⁴/photon/s or cm⁴ s.

In our measurement, the incident radiation is 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 the repetition rate of the 800 nm laser is 8 ns, 4 mm, 1.3 mrad, and 10 Hz, respectively. The laser beam was focused with a $f = 20$ cm lens and passed through a 1 cm path quartz cuvette filled with the solution sample. 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 the self-focusing or self-defocusing effects inside the sample, the sample cell was 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 totally captured by the power meter, so that the influence of the possible change of the beam structure could be avoided.

After measuring the relationship between input and output laser beam intensity, eq 2 was used to fit the experimental data and thus determine the corresponding two-photon absorption coefficient β . To compare the TPA cross section of these two series of materials without interference from solvent polarity effects, the same solvent, tetrahydrofuran (THF), was used for the TPA characterization of all these materials.

Results and Discussion

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 divided by molecular weight. Using these data, some well-defined molecular structure/two-photon property relationships at 800 nm can be formulated for the dyes containing pyridine acceptors. Some of the more important relationships are depicted in the flowcharts illustrated in Figures 9 and 10. It must be remembered that valid absolute structure/property relationships (comparisons of two-photon absorption cross sections) can only be ascertained for those molecules which have their two-photon absorption peak at approximately the same wavelength. If the two-photon peak is 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 structure/property relationships deduced from the experimental data in this study are most valid at 800 nm. This wavelength was chosen since 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. It also should be remembered 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 section.

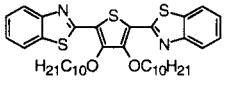
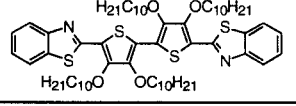
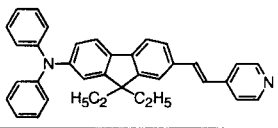
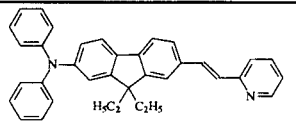
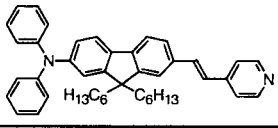
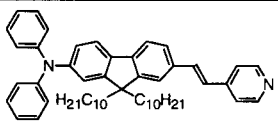
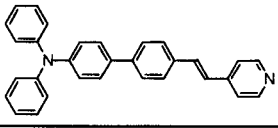
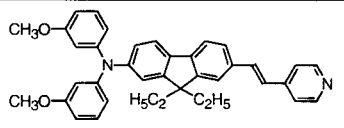
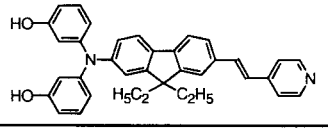
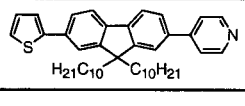
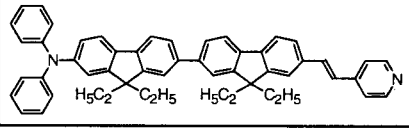
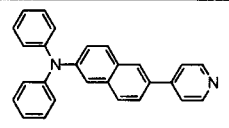
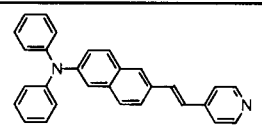
Regardless of the absolute mechanisms involved, certain structure/property relationships can be observed from the measured values of the effective two-photon cross sections using nanosecond pulses.

The single example molecule where a relatively weak donor was used in conjunction with a fluorene bridge is compound **22**. In this case the weak thiophene donor was found to be of insufficient activity to produce a TPA cross section in the desired range. If the stronger donor diphenyl amino group is substituted for the thiophene ring and the conjugation length is extended via the addition of a double bond between the pyridine acceptor and the fluorene bridge (compound **14**) the TPA cross section at 800 nm is increased by almost 2 orders of magnitude. If one changes the pendant alkyl groups from *n*-decyl to ethyl and then extends the conjugation to first produce the 2-pyridyl compound **12** followed by the 4-pyridyl derivative **11**, an overall similar result is obtained. The evaluation of the effects of planarity are illustrated by the comparison of compound **15** containing the less planer biphenyl bridge with the fluorene bridged compound **11**. An increase in 248% in the experimentally determined TPA cross section is observed for the fluorene-containing compound.

The role of the pendant side chains initially placed into the molecular design was to facilitate solubility, and its influence on the experimental TPA cross section was found to be greater than initially expected. It was observed that as the pendant alkyl chain length was increased from ethyl (compound **11**) to *n*-hexyl (compound **13**) to *n*-decyl (compound **14**) the TPA cross section was increased by approximately 19% (Figure 10). The reason for the increase could be due to the steric hindrance of the longer chain alkyl groups, which would inhibit aggregate (and possible excimer) formation. This aggregate formation was observed earlier¹² for compound **14** in a plot of predicted upconverted fluorescence intensities compared to the observed intensities as a function of concentration.

The magnitude of the effective TPA cross section can also be increased for the fluorene bridged compounds by increasing the electron density on the diphenylamino donor group. The effect observed was somewhat unexpected since the electron-donating functional groups were not in a position on the phenyl rings which was in direct conjugation with the amine nitrogen. The TPA cross section increased approximately 18% in going from the unsubstituted diphenyl amino compound **11** through the dihydroxy compound **20** to the dimethoxy compound **17** (Figure 10). There are obviously other factors which

Table 1. Optical Properties of the Chromophores at 800 nm in THF

Chromophore	λ_{\max} (nm) Linear Abs. (Upconv. Em.)	β cm / GW at 0.02 mol/L	σ_2' ($\times 10^{-48}$ cm ⁴ ·sec ph-molecule)	σ_2'/MW ($\times 10^{-50}$ cm ⁴ ·sec·mole ph-molecule·g)
 1	390 (465)	0.2	4.90	0.7
 2	430 (521)	1.4	28.5	2.7
 11	388 (488)	4.7	97.0	19.7
 12	384.5 (478)	4.7	79.4	16.1
 13	389 (494)	5.1	106.1	17.5
 14	390 (492)	5.6	115.6	16.1
 15	367 (485)	1.9	39.0	9.2
 17	386 (488)	5.6	114.8	20.8
 20	392 (500)	5.0	103	19.6
 22	345 (410)	0.06	1.31	0.2
 24	383.5 (492)	3.8	79.4	11.1
 28	347 (453)	0.6	12.9	3.5
 30	388 (488)	3.3	68.4	17.2

need to be considered since the dihydroxy compound **20** has a smaller TPA cross section than the dimethoxy

analogue **17**. This is contrary to what was initially expected if there were no other factors involved since

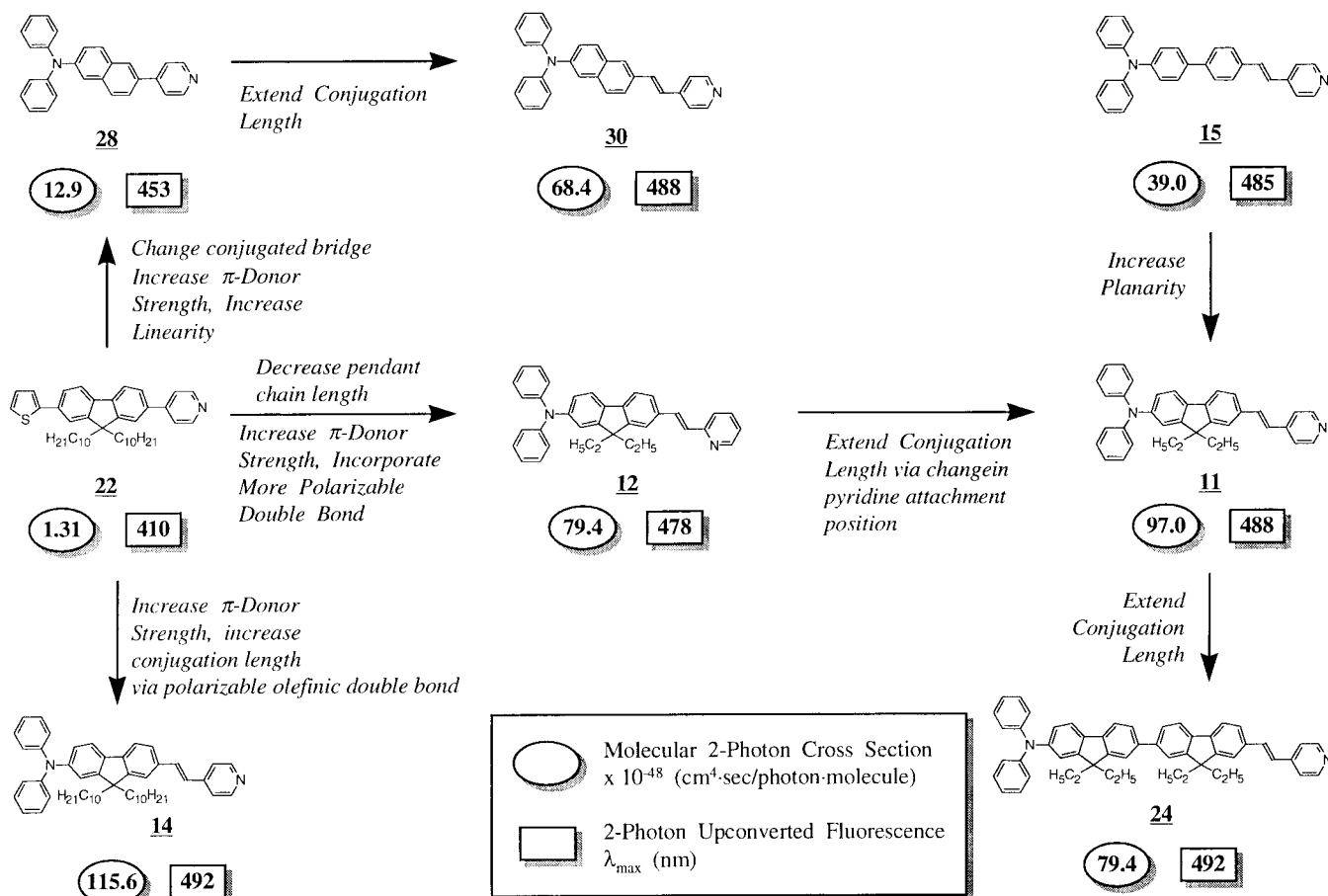


Figure 9. Flowchart of compounds.

the hydroxy group is normally thought to be a stronger π electron donor than the methoxy group. This behavior might again be due to increased aggregation in solution in this case brought about by the hydrogen-bonding ability of the hydroxy groups with the pyridyl units.¹³ If one looks at what happens when the conjugation is extended by the incorporation of a second fluorene ring system into the bridging unit, it is seen that there is actually a reduction in the effective TPA cross section (Figure 9). It is postulated that this is due to decreased effective conjugation between the donor and acceptor groups brought about by increased rotation of the adjacent fluorene groups, causing the molecule as a whole to be less planar.

Since the planarity of the ground-state geometry seems to be critical in attaining optimized TPA cross section values, an alternate π bridging group, 2,6-naphthyl, was investigated. When the pyridine electron acceptor group was attached directly to the bridging naphthyl group in compound **28**, a relatively small value for the cross section was obtained. The addition of a more polarizable double bond between the naphthyl bridge and the pyridyl acceptor (compound **30**) brings about a 5-fold increase in cross section (Figure 9), and this value is somewhat smaller than the measured TPA cross section of compound **11**, the fluorene analogue which has the most comparable structure.

The measured values for the TPA cross section of compound **14** vary substantially with the polarity of the

solvent. For example, the measured value for σ_2' in THF is found to be $115.3 \text{ cm}^4 \text{ s}/\text{photon molecule}$ and $152.5 \text{ cm}^4 \text{ s}/\text{photon molecule}$ when measured in benzene. Further discussion about the variation of cross section with solvent polarity is beyond the scope of this paper and will be presented in a separate publication.

Conclusions

A careful characterization via nonlinear transmission experiments has provided effective two-photon absorption data for two new families of nonlinear optical materials. The nonlinear transmission method was chosen as a characterization technique for its simplicity and direct nature. Comparison of the experimental data helps to define some specific molecular structure/two-photon property relationships for the new chromophores, although there are some questions left unanswered. It appears that several structural factors are critical in order to obtain large cross sections at 800 nm. In general, for the types of bridges studied, the structural elements which appear most important all help to increase the effective conjugation between the donor and acceptor. In type 1 chromophores, when a second thiophene ring is added to the bridge to increase the conjugation length, the TPA cross section is increased, but the upconverted emission is also shifted toward the red. It was postulated that the incorporation of additional thiophene groups will shift the TPA peak away from 800 nm. Work on this family of materials was discontinued in favor of investigating nonthiophene aromatic bridges. In the aromatic/olefinic bridges stud-

(13) Beezer, A. E.; Hawksworth, W. A.; Orban, M.; Tyrrell, H. J. V. *J. Chem. Soc., Faraday Trans. 1*, **1977**, 73 (9), 1326.

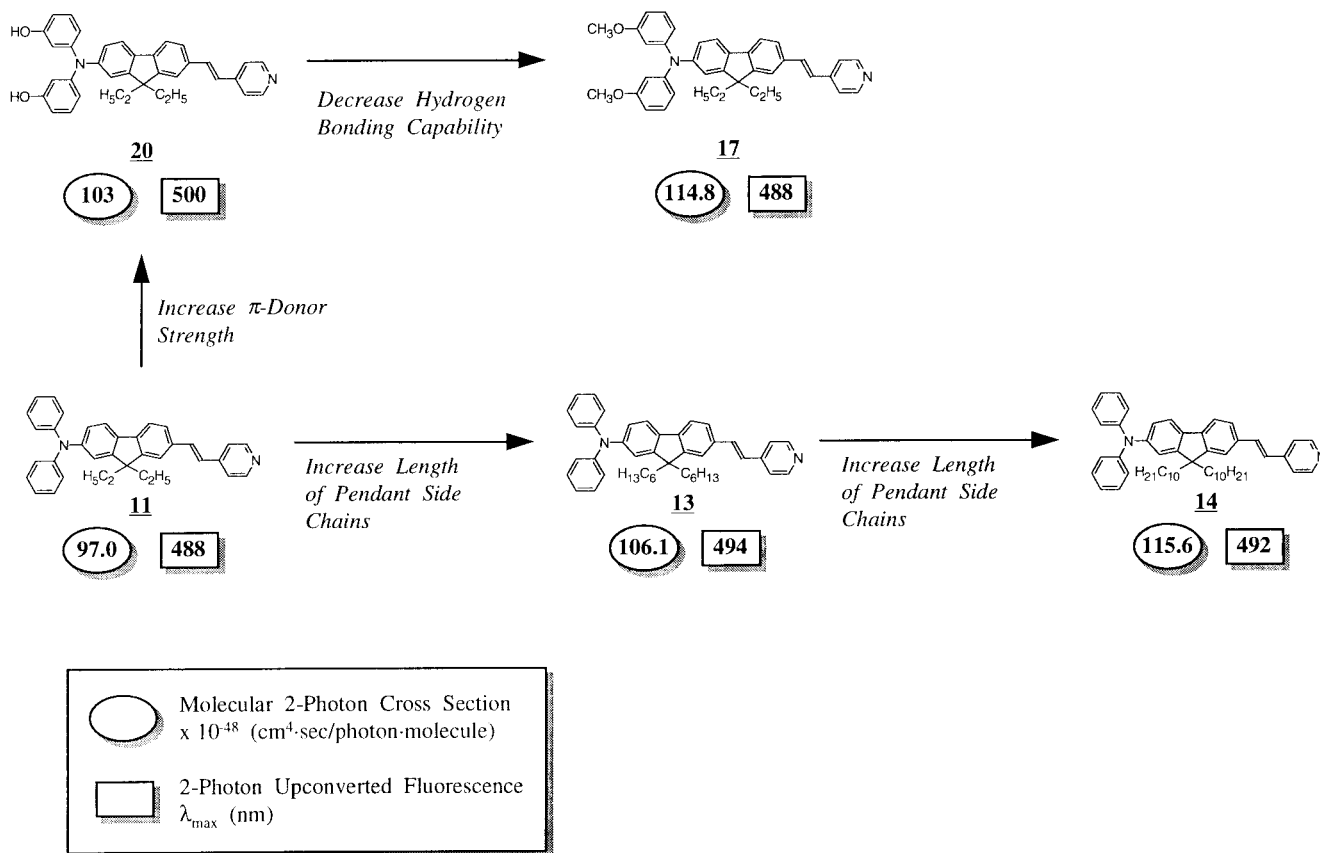


Figure 10. Flowchart of compounds (*continued*).

ied, planarity seems to be critical in obtaining high values of the two-photon cross section. Donors appear to need to have relatively strong donating activity to maximize cross section. Pyridine acceptors when coupled with diarylamino donors appear to be of the correct strength to allow the two-photon absorption peak to fall close to 800 nm. Changing the aromatic bridge from biphenyl to fluorene to naphthalene seems to have little effect on the position of two-photon absorption and upconverted fluorescent emission, although there are substantial differences in the magnitude of the TPA cross section. Comparison of the experimentally determined cross sections in different solvents indicate that in all cases the cross sections measured in nonpolar solvent were larger than the values determined in more polar media. This type of solvatochromatic behavior is reportedly observed for fluorescent dyes where the fluorescence intensity of a molecule in solution is reduced via solvation by a polar solvent. This effect is important in molecules which form polar charge transfer excited states which can interact strongly with polar solvents, thus facilitating nonradiative routes for excited-state relaxation.¹³ This has been studied previously¹⁴ to some extent for compound **14** and is thought to be due to a combination of factors. The amount of aggregate formation and the interaction of solvent with the excited state seem to be critical factors in the understanding of these systems. Work is currently underway to further investigate these factors.

A summary of the experimental data indicates that two molecules, compounds **14** and **17**, stand out as

having the largest effective two-photon cross sections, σ_2' and the largest σ_2'/MW , respectively. It appears that the addition of moderately long electron-donating alkyl pendants to the fluorene bridging group not only imparts additional solubility to the molecules but also increases the apparent measured cross section. The addition of strongly donating alkyl ether groups to the donor end of the molecule, even if not in direct conjugation with the amine nitrogen, produces a large increase in cross section as a function the relatively small increase of molecular weight. Additional research is in progress to synthesize molecules which exhibit even higher activity using a combination of these molecular structural elements.

It still remains to be shown what role excited state absorption (ESA) plays for these molecules in the total process mechanism and what effects it has on the experimental values obtained for the effective two-photon cross section using nanosecond pulses. This problem is currently being addressed with additional experimental investigations using femtosecond time-resolved techniques.

Experimental Section

Fluorene, *n*-butyllithium, 1-bromodecane, iodine, bromine, 4-bromopyridine hydrochloride, 2-bromothiophene, triphenylphosphine, 2-thienyllithium, tributyltin chloride, tetrakis(triphenylphosphine)palladium(0), magnesium sulfate, 4-vinylpyridine, potassium iodide, potassium hydroxide, sodium hydroxide, potassium carbonate, bromoethane, *m*-anisidine, and 3-bromoanisole were purchased from Aldrich Chemical Co. and used without further purification. Bis(triphenylphosphine) palladium(II) chloride, palladium acetate, and tri-*o*-tolylphosphine were purchased from Strem Chemicals. Bis-

(14) Wehry, E. L. In *Practical Fluorescence*; Guilbault, G. G., Ed.; Marcel Dekker: New York, 1990; pp 141–142.

(dibenzylideneacetone) palladium(0) was purchased from Lancaster Synthesis, Inc. Trimethylsilyl polyphosphate (PPSE) was purchased from Fluka Chemical Company. Celite 545 and Sodium bisulfite were acquired from Fisher Scientific.

The silica gel (63–200 μ , dry column) and alumina (63–200 μ) used in column chromatography were purchased from Scientific Adsorbents, Inc.

3,4-Bis(decyloxy)-2,5-bis(benzothiazol-2-yl)thiophene(1). This compound was synthesized by the scheme in Figure 1 according to the published procedure.¹⁵

3,4-Bis(decyloxy)-5-(benzothiazol-2-yl)thiophene-2-carboxylic acid. This compound was synthesized in 41% yield using a previously published procedure.¹⁶

2-Bromo-3,4-bis(decyloxy)-5-(benzothiazol-2-yl)thiophene. To a magnetically stirred mixture of the monocarboxylic acid (17.2 g, 29.97 mmol), potassium carbonate (8.4 g, 60.78 mmol), and water (300 mL) held at 45 °C was added bromine (8.4 g, 52.56 mmol) over 15 min. After 45 min at 50 °C, the mixture was cooled to room temperature and treated with 10% sodium hydroxide, water, and saturated sodium chloride solution. After drying, the toluene solution was concentrated and the residual oil was chromatographed over 200 g of silica gel. Elution with 1/3 toluene/heptane gave an oily product which solidified upon standing with methanol to give 16.85 g (91% yield). Mp = 42–43 °C. MS: m/z 480, 481, 482 ($M^+ - C_9H_{19}$). Anal. Calcd for $C_{31}H_{46}NO_2S_2$: C, 61.16; H, 7.62; Br, 13.14; N, 2.30; S, 10.51. Found: C, 60.85; H, 7.70; Br, 13.48; N, 2.29; S, 10.42.

3,4,3',4'-Tetradecyloxy-5,5'-bis(benzothiazol-2-yl)-2,2'-bithiophene (2). A solution of 2-bromo-3,4-bis(decyloxy)-5-(benzothiazol-2-yl)thiophene (12.2 g, 20.04 mmol) and bis-tributyltin (5.8 g, 10.00 mmol) in dioxane (100 mL, freshly distilled from sodium after treatment with potassium hydroxide) was degassed by bubbling nitrogen through the solution for 20 min. Under nitrogen, tetrakis(triphenylphosphino)palladium (0.468 g, 0.40 mmol) was added and the mixture was heated at 100 °C for 20 h. After cooling, pyridine (5 mL) was added and the resulting mixture allowed to stand for 1 h. The separated solids were filtered, and the filtrate was diluted with an equal volume of water. The mixture was extracted with an equal volume of toluene, dried over magnesium sulfate, and concentrated. The residue was combined with the initial solids and chromatographed over 250 g of silica gel. Elution with 3/1 and 2/1 heptane/toluene gave the desired product which was recrystallized from heptane to give 7.02 g (66.5% yield). Mp = 93.9–95 °C. MS: m/z 916 ($M^+ - C_{10}H_{20}$). Anal. Calcd for $C_{62}H_{92}N_2O_4S_4$: C, 70.36; H, 8.77; N, 2.65; S, 12.10. Found: C, 69.98; H, 8.90; N, 2.59; S, 11.98.

General Synthetic Procedure for 2,7-Dibromo-9,9-dialkyl-9H-fluorenes (3–5). A mixture of 2,7-dibromo-9H-fluorene (1 equiv), potassium iodide (0.1 equiv), finely powdered KOH (5 equiv), and DMSO (100 mL) was mechanically stirred under nitrogen in a three-necked round-bottomed flask. The flask was cooled in an ice water bath before adding four batches of the bromoalkyl (2.6 equiv). After each addition, the internal temperature rose sharply. Once the last aliquot was completed, the reaction was stirred for 4 h at room temperature before water (200 mL) was added. The solid was filtered off and dried in a desiccator equipped with P_2O_5 under vacuum for 16 h.

2,7-Dibromo-9,9-diethyl-9H-fluorene (3). The product was recrystallized in hexane to produce white crystals (mp 156–158 °C) in 80.92% yield. MS: m/z 378, 380, 382 (M^+), 349, 351, 353 ($M - C_2H_5$), 299, 301 ($M-Br$), 270, 272 (349- Br). Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.72; H, 4.24; Br, 42.04. Found: C, 53.79; H, 4.22; Br, 42.22.

2,7-Dibromo-9,9-di-*n*-hexyl-9H-fluorene (4). The product was recrystallized from ethanol to produce 2,7-dibromo-9,9-di-*n*-hexyl-9H-fluorene as white crystals (mp 67.2–70.0 °C)

in 69% yield. MS: m/z 490, 492, 494 (M^+), 405, 407, 409 ($M - C_6H_{13}$). Anal. Calcd for $C_{25}H_{32}Br_2$: C, 60.99; H, 6.55; Br, 32.46. Found: C, 60.78; H, 6.95; Br, 33.15.

2,7-Dibromo-9,9-di-*n*-decyl-9H-fluorene (5). The product was recrystallized from ethanol to produce 2,7-dibromo-9,9-di-*n*-decyl-9H-fluorene as white crystals (mp 38.1–38.4 °C) in 82.79% yield. MS: m/z 602, 604, 606 (M^+), 461, 463, 465 ($M - C_{10}H_{21}$), 382, 384 (461 - Br). Anal. Calcd for $C_{33}H_{48}Br_2$: C, 65.56; H, 8.00; Br, 26.44. Found: C, 64.99; H, 8.21; Br, 27.25.

General Synthetic Procedure for Diphenylamine Coupling with an Arylbromide 7–10, 17, 18. Diphenylamine (1 equiv) and toluene (56 mL, dried over $CaCl_2$, distilled and degassed with nitrogen for 15 min) were added to a three-necked round-bottomed flask equipped with a magnetic stir bar, thermometer, reflux condenser, and an addition funnel containing *n*-butyllithium (1.01 equiv). The solution was cooled in a dry ice/acetone bath until the internal temperature was –5 °C. The *n*-butyllithium was added dropwise so that the temperature never rose above 0 °C. A white solid formed immediately. The reaction mixture was stirred at –5 °C for 90 min. While the reaction temperature was maintained at –5 °C, tri-*o*-tolylphosphine (0.2 equiv), arylbromide (1 equiv), and bis(dibenzylideneacetone)palladium(0) catalyst (0.02 equiv) were added. The ice bath was removed and the mixture was heated in an oil bath for 72 h at an internal temperature of 70 °C.

***N,N*-Diphenyl-7-bromo-9,9-diethyl-9H-fluorene-2-amine (7):** colorless cubic crystals (mp = 141.5–142.5 °C) in 18% yield. MS: m/z 467, 469 (M^+). Anal. Calcd for $C_{29}H_{26}BrN$: C, 74.36; H, 5.59; N, 2.99; Br, 17.06. Found: C, 74.37; H, 5.90; N, 3.30; Br, 17.10.

***N,N*-Diphenyl-7-bromo-9,9-di-*n*-hexyl-9H-fluorene-2-amine (8)** was purified by column chromatography using silica gel and a mixture of 9/1 hexane/toluene as eluent to afford the product as an oil in 20% yield. MS: m/z (M^+). Anal. Calcd for $C_{37}H_{42}BrN$: C, 76.53; H, 7.29; N, 2.41; Br, 13.76. Found: C, 76.66; H, 7.43; N, 2.92; Br, 13.82.

***N,N*-Diphenyl-7-bromo-9,9-di-*n*-decyl-9H-fluorene-2-amine (9).** The product was purified by column chromatography on alumina using hexane as the eluent to produce a light brown oil in 35.25% yield. MS: m/z 691, 693 (M^+). Anal. Calcd for $C_{45}H_{58}BrN$: C, 78.01; H, 8.44; N, 2.02. Found: C, 79.32; H, 8.38; N, 1.51.

***N,N*-Diphenyl-*N*-[4-(4-bromophenyl)phenyl]amine (10).** The product was purified by column chromatography on alumina using hexane as eluent and then recrystallized from hexane to produce crystals (mp = 125–127 °C) in 35% yield. MS: m/z 399, 401 (M^+), 320 ($M - Br$). Anal. Calcd for $C_{24}H_{18}BrN$: C, 72.01; H, 4.53; N, 3.49; Br, 19.96. Found: C, 72.05; H, 4.56; N, 3.36; Br, 19.79.

***N,N*-Bis(3-methoxyphenyl)-*N*-{9,9-diethyl-7-[2-(4-pyridyl)-1-ethenyl]-9H-2-fluorenyl}amine (17).** The product was purified by three column chromatographies; the first used alumina and toluene as eluent, the second used alumina and a 50/50 cyclohexane/toluene mixture as eluent, and the third used silica gel and a 95/5 toluene/THF mixture as eluent. The resulting dark green oil was afforded in 58.10% yield. MS: m/z 552 (M^+), 523 ($M - C_2H_5$), 508 (523 - CH_3). Anal. Calcd for $C_{38}H_{36}N_2O_2$: C, 82.58; H, 6.57; N, 5.07, O, 5.78. Found: C, 83.26; H, 6.94; N, 4.55, O, 5.17.

***N,N*-Bis(3-methoxyphenyl)-*N*-(7-bromo-9,9-diethyl-9H-2-fluorenyl)amine (18).** The product was purified by column chromatography on silica gel using a 90/10 hexane/THF mixture as eluent to afford a light brown oil in 34.94% yield. MS: m/z 527, 529 (M^+), 498, 500 ($M - C_2H_5$), 483, 485 (498 - CH_3). Anal. Calcd for $C_{31}H_{30}NO_2Br$: C, 70.46; H, 5.72; N, 2.65, O, 6.05. Found: C, 75.23; H, 6.74; N, 2.47, O, 6.12.

General Synthetic Scheme for Coupling Vinylpyridine with an Aryl Bromide 11–16, 20. The aryl bromide (1 equiv), tri-*o*-tolylphosphine (0.4 equiv), triethylamine (30 mL, degassed with nitrogen for 15 min), vinylpyridine (2 equiv), and palladium(II) acetate (0.05 equiv) were added to a single-necked round-bottomed flask equipped with a magnetic

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stirrer and reflux condenser. The solution was heated at reflux by means of an oil bath under nitrogen for 16 h.

The solvent was removed under reduced pressure and the residue dissolved in methylene chloride. The organic layer was washed three times with water, dried over anhydrous MgSO_4 , filtered, and concentrated.

***N,N*-Diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-diethyl-9*H*-fluoren-2-amine (11).** The product was isolated by column chromatography on alumina using toluene as eluent. The resulting solid was then stirred with hexane to remove trace impurities and then filtered. The yellow solid (mp = 192.5–194.0 °C) was afforded in 49.18% yield. MS: m/z 492 (M^+), 463 ($\text{M} - \text{C}_2\text{H}_5$), 168 ($\text{C}_6\text{H}_5 - \text{N} - \text{C}_6\text{H}_5$). Anal. Calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2$: C, 87.77; H, 6.55; N, 5.68. Found: C, 86.95; H, 6.39; N, 5.58.

***N,N*-Diphenyl-7-[2-(2-pyridinyl)ethenyl]-9,9-diethyl-9*H*-fluoren-2-amine (12).** The product was isolated by column chromatography on alumina using a 1/1 heptane/toluene mixture as eluent. The solid was further purified by recrystallization from 1/1 heptane/ethyl acetate to afford the product (mp = 171–173 °C) in 39% yield. Anal. Calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2$: C, 87.77; H, 6.55; N, 5.69. Found: C, 87.5; H, 6.85; N, 5.61.

***N,N*-Diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-*n*-hexyl-9*H*-fluoren-2-amine (13).** The product was purified by column chromatography using alumina and a mixture of 75/25 methylene chloride/heptane and then by recrystallization in methanol to produce yellow crystals (mp = 145.0–146.9 °C) in 46% yield. MS: m/z 604 (M^+), 519 ($\text{M} - \text{C}_6\text{H}_{13}$). Anal. Calcd for $\text{C}_{44}\text{H}_{48}\text{N}_2$: C, 87.37; H, 7.99; N, 4.63. Found: C, 87.27; H, 8.22; N, 4.43.

***N,N*-Diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-*n*-decyl-9*H*-fluoren-2-amine (14).** The product was purified by column chromatography on silica gel using a 85/15 hexane/ethyl acetate mixture as eluent to produce a yellow oil in 59.45% yield. The oil, upon standing for several days, gradually solidified to give a waxy solid (mp = 88.4–89.3 °C). MS: m/z 716 (M^+), 576 ($\text{M} - \text{C}_{10}\text{H}_{20}$), 358 (M^{2+}). Anal. Calcd for $\text{C}_{52}\text{H}_{64}\text{N}_2$: C, 87.10; H, 9.00; N, 3.90. Found: C, 87.17; H, 9.45; N, 3.35.

***N,N*-Diphenyl-*N*-(4-{4-[2-(4-pyridyl)-1-ethenyl]phenyl}-phenyl)amine (15)** was purified by column chromatography using alumina and a mixture of 75/25 hexane/methylene chloride to afford a white solid (mp = 219.0–220.5 °C) in 45% yield. MS: m/z 424 (M^+), 212 (M^{2+}). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_2$: C, 87.70; H, 5.58; N, 6.60. Found: C, 87.39; H, 5.84; N, 6.42.

4-[2-(7-Bromo-9,9-diethyl-9*H*-2-fluorenyl)-1-ethenyl]-pyridine (16). The product was purified by column chromatography using alumina and a 98/2 toluene/acetone mixture as eluent to afford a yellow solid in 35.08% yield. MS: m/z 403, 405 (M^+), 374, 376 ($\text{M} - \text{C}_2\text{H}_5$), 295 (374 – Br). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{NBr}$: C, 71.29; H, 5.48; N, 3.46. Found: C, 71.96; H, 5.20; N, 3.23.

3-[(9,9-Diethyl-7-[2-(4-pyridyl)-1-ethenyl]-9*H*-2-fluorenyl]-3-hydroxyanilino]phenol (20). The product was roughly purified by a short column chromatography on silica gel using a 75/25 ethyl acetate/hexane mixture as eluent to afford a yellow oil. The oil was then stirred in hexane to produce a yellow solid which was then filtered. The solid was purified by column chromatography on silica gel using a 80/13/7 toluene/ CNCH_3 /THF mixture as eluent. Once the less polar impurities had been collected, the eluent was switched to a 67/22/11 toluene/ CNCH_3 /THF mixture. The product was then recrystallized twice using toluene to produce yellow crystals (mp = 258.2–260.0 °C with decomposition) in 27.74% yield. MS: m/z 524 (M^+), 495 ($\text{M} - \text{C}_2\text{H}_5$). Anal. Calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_2$: C, 82.41; H, 6.15; N, 5.34, O, 6.10. Found: C, 82.48; H, 6.13; N, 5.17, O, 6.29.

3-[(7-Bromo-9,9-diethyl-9*H*-2-fluorenyl)-3-hydroxyanilino]phenol (19). A solution of *N,N*-bis(3-methoxyphenyl)-*N*-(7-bromo-9,9-diethyl-9*H*-2-fluorenyl)amine (18) (14.97 g, 28.33 mmol) and methylene chloride (100 mL, dried over CaCl_2 and freshly distilled) was magnetically stirred in a three-necked round-bottomed flask equipped with a nitrogen line,

thermometer, and an addition funnel filled with boron tribromide (127.5 mL of a 1M solution in methylene chloride, 127.49 mmol). The solution was cooled to –55 °C in a dry ice/acetone bath and the BBr_3 was slowly added. The mixture immediately turned black. The funnel was rinsed with additional methylene chloride (10 mL) and the reaction was stirred for 16 h at 25 °C.

The mixture was then poured over a slurry of ice water and stirred while nitrogen bubbled through the solution to evaporate the methylene chloride. Once the water warmed to room temperature, a NaOH solution (36 g in 100 mL of water) was added and the mixture was warmed to 65 °C for 1 h. The black oil below the water layer went into solution. Once the solution had cooled back to room temperature, a dilute HCl solution was added and the mixture was carefully adjusted to pH = 7. A cream-colored solid fell out of solution and was then filtered and dried in a desiccator under high vacuum. The product 19 was purified by column chromatography on silica gel using a 75/25 hexane/THF mixture as eluent to afford the product (mp = 159–162 °C) in 87.02% yield. MS: m/z 499, 501 (M^+), 470, 472 ($\text{M} - \text{C}_2\text{H}_5$). Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{NO}_2\text{Br}$: C, 69.60; H, 5.24; N, 2.80, O, 6.39; Br, 15.97. Found: C, 69.68; H, 5.58; N, 2.24, O, 6.99; Br, 15.37.

4-(7-Bromo-9,9-di-*n*-decyl-9*H*-fluorenyl)pyridine (21). 4-(Tri-*n*-butylstannyl)pyridine (8.30 g, 22.56 mmol) was added directly to a single-necked round-bottomed flask equipped with a condenser and a magnetic stir bar that had been dried in an oven at 110 °C overnight. 2,7-Dibromo-9,9-di-*n*-decyl-9*H*-fluorene (15.00 g, 24.81 mmol) was weighed into a beaker and dissolved in dry toluene (65 mL, previously degassed with nitrogen). The fluorene solution was pipetted into the round-bottomed flask and the beaker rinsed with two 5 mL portions of degassed toluene. $\text{Pd}(\text{PPh}_3)_4$ (0.26 g, 0.22 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (1.58 g, 2.25 mmol), and triphenylphosphine (1.30 g, 4.96 mmol) were added to the reaction flask, and the solution was heated at reflux until it turned black.

The reaction mixture was cooled to room temperature, the toluene removed under reduced pressure, and the residue dissolved in hexane. The hexane solution was stirred vigorously with 100 mL of a 2% aqueous KF solution for 3 h. The organic layer was separated, washed twice with equal volumes of water, dried over anhydrous MgSO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel using a 85/15 hexane/THF mixture as eluent. The purified compound was isolated in 58.5% yield as a light yellow oil. MS: m/z 601, 603 (M^+), 460, 462 ($\text{M} - \text{C}_{10}\text{H}_{21}$), 381 (460 – Br). Anal. Calcd for $\text{C}_{38}\text{H}_{52}\text{NBr}$: C, 75.72; H, 8.70; N, 2.32. Found: C, 69.01; H, 8.27; N, 1.46.

4-(9,9-Di-*n*-decyl-7-(2-thienyl)-9*H*-2-fluorenyl)pyridine (22). 4-(7-Bromo-9,9-di-*n*-decyl-9*H*-fluorenyl)pyridine (2.32 g, 3.85 mmol) was weighed directly into a single-necked round-bottomed flask equipped with a magnetic stirrer and condenser which had been dried in an oven at 130 °C overnight. Toluene (20 mL, dried over CaCl_2 and freshly distilled) and 2-(tri-*n*-butylstannyl)thiophene (1.47 mL, 4.62 mmol) were added to the flask and the solution was degassed with nitrogen for 15 min. Tetrakis(triphenylphosphine)-palladium(0) (0.34 g, 0.29 mmol) was added and the solution was heated at reflux for 16 h under nitrogen. The reaction was cooled to room temperature and the toluene was removed under reduced pressure. The product was isolated by column chromatography on silica gel using a 90/10 hexane/THF mixture as eluent to produce a yellow oil in 72.38% yield. If the oil was allowed to stand at room temperature, it slowly solidified into a pale yellow waxy solid (mp = 58–61 °C). MS: m/z 605 (M^+), 464 ($\text{M} - \text{C}_{10}\text{H}_{21}$). Anal. Calcd for $\text{C}_{42}\text{H}_{55}\text{NS}$: C, 83.25; H, 9.15; N, 2.31. Found: C, 83.34; H, 8.89; N, 2.31.

4-(9,9,9'-Tetraethyl-7'-(diphenylamino)-2',7'-bifluorenyl-2-yl)vinylpyridine (24). To a solution of *N,N*-diphenyl-7-bromo-9,9-diethyl-9*H*-fluorene-2-amine (7) (7.02 g, 15 mmol) in THF (75 mL), cooled in dry ice/ethanol to –60 °C was added *n*-butyllithium (11 mL of a 1.6M solution in hexanes, 17.6 mmol) and the mixture was stirred for 45 min. A solution of tributyltin chloride (3.8 mL, 14 mmol) in THF (10 mL) was

then added and the mixture was stirred outside the bath overnight. After cooling in an ice bath, a solution of potassium fluoride was added, and the mixture stirred for 1 h and was filtered. The filtrate was diluted with toluene, and the organic phase was dried and concentrated to yield 11.78 g of the organotin **23** as an oil. MS: m/z 675, 677, 679 (M^+). This oil was dissolved in toluene [65 mL], mixed with 4-((9,9-diethyl-7-bromofluoren-2-yl)viny)pyridine (**16**) (5.45 g, 13.5 mmol), degassed, and treated with bis(triphenylphosphino)palladium(II) chloride (0.525 g, 0.75 mmol). The mixture was then held at 100 °C for 24 h, cooled, and treated with a solution of potassium fluoride. The precipitated tin fluoride was filtered off, the filtrate was concentrated, and the residue was transferred to a column of 400 g of alumina. The product came out on elution with toluene. All the product was transferred to a column of 120 g of silica gel, and the column was eluted with 5 to 15% ethyl acetate/toluene, to yield (4.76 g (49% yield) of the product after trituration with toluene (mp 152.9–154.5 °C). MS: m/z 712 (M^+). Recrystallizations from 2/1 heptane/toluene raised the melting point to 220.2–221.1 °C. Anal. Calcd for $C_{53}H_{58}N_2$: C, 89.28; H, 6.79; N, 3.93. Found: C, 88.98; H, 6.74; N, 3.77.

6-Bromo-*N*-phenyl-2-naphthylamine (26). A mixture of 6-bromo-2-naphthol (16.4 g, 0.074 mol), aniline (25 mL, 0.27 mol), xylene (25 mL), and *p*-toluenesulfonic acid monohydrate (2.7 g, 0.014 mol) was heated to reflux under nitrogen. A portion of xylene was distilled off to raise the reflux temperature to 190 °C and the reaction temperature was maintained at 190 °C for 5 h. After cooling to 85 °C, anhydrous sodium acetate (3.7 g, 0.045 mol) and ethanol (100 mL) were added. The mixture was heated to reflux and the solution was cooled to 5 °C. The cooled slurry was filtered, and the solids were washed with ethanol (50 mL) and aspirated dry. The solids were then reslurried in warm water (150 mL), filtered, and washed with water to give 19.3 g (88% yield) of colorless solids (mp = 126.2–128.3 °C).

A sample was recrystallized twice from heptane/ethyl acetate (19/1) (mp = 131–133 °C). MS: m/z 297, 299 (M^+). Anal. Calcd for $C_{16}H_{12}NBr$: C, 64.45; H, 4.06; N, 4.70; Br, 26.80. Found: C, 64.36; H, 4.02; N, 4.61; Br, 27.04.

6-(4-Pyridyl)-*N*-phenyl-2-naphthylamine (27). A mixture of bromonaphthylamine (2.98 g, 0.01 mol), 4-(tributylstannyl)pyridine (4.6 g, 0.125 mol), and toluene (10 mL) was degassed by bubbling nitrogen through for 10 min. Bis(dibenzylideneacetone)palladium(0) (0.24 g, 0.42 mmol) and triphenylarsine (0.48 g, 1.56 mmol) were then added. The mixture was maintained at 110 °C for 18 h and then cooled to room temperature. A solution of potassium fluoride (1 g) in water was then added, the mixture was stirred for 1 h, diluted with toluene, and filtered to remove the insoluble organotin fluoride (1.38 g). The toluene filtrate was dried ($MgSO_4$) and

concentrated, and the residue was chromatographed over silica gel (125 g). Elution with toluene/heptane (1600 mL) returned unreacted bromonaphthylamine (1.03 g, 35% recovery) (mp = 128–129.6 °C). Elution with 10% THF/toluene (1000 mL) brought 0.82 g (28% yield on bromonaphthylamine) of the product (mp = 159–160.2 °C) (toluene/heptane). The yield is 42% after adjusting for recovery of starting bromo compound. A sample was sublimed under vacuum (1 mm) in a 160 °C bath for analysis. MS: m/z 296 (M^+). Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.23; H, 5.58; N, 9.71.

6-(4-Pyridyl)-*N,N*-diphenyl-2-naphthylamine (28). A mixture of 6-(4-pyridyl)-*N*-phenylnaphthylamine (2.21 g, 7.46 mmol), iodobenzene (3.75 g, 18 mmol), potassium carbonate (5.0 g, 36.0 mmol), copper/bronze (0.38 g, 5.9 mmol), 18-crown-6 (0.38 g, 1.4 mmol), and 1,2-dichlorobenzene (12 mL) was heated to 182 °C in an oil bath under nitrogen and held at that temperature for 3 h. The reaction was cooled, diluted with toluene, and filtered. The filtrate was chromatographed over 150 g of silica gel and eluted with toluene. The fractions containing the product were combined and concentrated, and residual solids were recrystallized from toluene/heptane to give 2.41 g (86% yield) (mp = 180.7–182.0 °C). MS: m/z 372 (M^+). Anal. Calcd for $C_{27}H_{20}N_2$: C, 87.07; H, 5.41; N, 7.52. Found: C, 87.33; H, 5.44; N, 7.17.

6-Bromo-*N,N*-diphenyl-2-naphthylamine (29). A mixture of 6-bromo-*N*-phenyl-2-naphthylamine (29.8 g, 0.1007 mol), iodobenzene (50 g, 0.245 mol), potassium carbonate (60 g, 0.434 mol), copper/bronze powder (4.0 g, 0.063 mol), 18-crown-6 (3.7 g, 0.014 mol), and 1,2-dichlorobenzene (100 mL) was kept at reflux (180–185 °C) for 3 h under nitrogen. After cooling and dilution with toluene, the slurry was filtered, and the filtrate was concentrated. The residual oil was chromatographed over 600 g of silica gel. After elution with hexanes to remove unreacted iodobenzene, elution with heptane and 10% toluene/heptane gave 28.65 g (77% yield) of product (mp = 135.8–137.4 °C). A sample was recrystallized twice from heptane (mp = 137.9–139.2 °C). MS: m/z 373, 375 (M^+), 421 ($M^+ - I$). Anal. Calcd for $C_{22}H_{16}NBr$: C, 70.59; H, 4.31; N, 4.09; Br, 21.35. Found: C, 69.23; H, 4.25; N, 3.61; Br, 20.56.

4-(6-*N,N*-Diphenylamino-2-naphthyl)-vinylpyridine (30). The residue was chromatographed over silica gel. Elution with 10% toluene/heptane gave 3.15 g (33.7% recovery) of unreacted bromo compound (mp = 128–130 °C). 10% THF/toluene eluted 4.15 g (42% yield) of the product (mp = 200.3–203.2 °C). Recrystallizations from 1/1 toluene/heptane raised the melting point to 202.0–204.5 °C. MS: m/z 318 (M^+). Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.31; H, 5.62; N, 6.70.

CM980036E