JOC Article

Diarylamino Groups as Photostable Auxofluors in 2-Benzoxazolylfluorene, 2,5-Diphenyloxazoles, 1,3,5-Hexatrienes, 1,4-Distyrylbenzenes, and 2,7-Distyrylfluorenes

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The relationship of structure to optical spectral properties was determined for five types of fluors in a search for an optimum-wavelength shifter to be used as part of the detection systems for high-energy particles from accelerators. In a search for photostable fluors to serve as waveshifters in plastic fibers it was found that the wavelengths of interest, absorption max 410 ± 10 nm and fluorescence emission max 480 ± 20 nm, along with other properties, such as high solubility and short fluorescence decay time, could be obtained from fluorophors composed of aromatic rings and vinyl groups only by using amino groups as auxochromes to give bathochromic shifts of wavelengths. Since primary, monoalkyl, and dialkylamino groups were not sufficiently photostable, a number of fluorophores bearing diarylamino groups were investigated. Syntheses of the fluors made use of the Buchwald amination, an improved version of the Emmons–Horner reaction, and other common reactions. The fluor types were the following: a 2-benzoxazolyl-7-(4-diarylamino)fluorene **7**, 2-(4-cyanophenyl)-5-(4-aminophenyl)oxazoles **14** and **20**, 1,3,5-hexatrienes **24a–d** and **26a–c**, 1,4-distyrylbenzenes **31d–g** and **32a–e**, and 2,7-distyrylfluorenes **40a,d–e**. The unsymmetrical fluors **7**, **14**, and **20** were not as bright as the best hexatrienes, distyrylbenzenes, and distyrylfluorenes, which were all symmetrical. Where the 1,6-diaryl-1,3,5-hexatrienes **24a–d** had high fluorescence quantum yield (Φ_f), the 1,1,6,6-tetraryl-1,3,5-hexatrienes **26a–c** had both lower ϵ and Φ_f. Where the 1,4-distyrylbenzenes **31d–g** had high Φ_f, the 1,4-bis(2-phenylstyryl)benzenes **32a–e** had $\Phi_f = 0$. Diarylamino groups as auxofluors conferred higher photochemical stability than dialkylamino groups on similar fluorophores. The 1,4-distyrylbenzenes **31d,e** and the 2,7-distyrylfluorenes **40d,e** had the most desirable properties overall, which included fast decay times of 2 ns. Computer simulations predicted absorption and emission wavelengths fairly well, but were of little help for the prediction of brightness, stability, Φ_f, or decay time.

Introduction

For decades the U.S. Department of Energy has supported research on accelerators, with which detectors of relativistic particles are essential. The components of detectors made of polystyrene (PS) tiles contain dissolved fluors that emit violet-to-blue light pulses (scintillations) derived from the impact of high-energy particles and photons. Because of the destruction of the light transmission of PS at shorter wavelengths by high flux levels of particles, the present approach is to change the wavelength of the light emitted to green for detection with green-sensitive photomultiplier tubes because the PS retains its light transmission at longer wavelengths. This is accomplished by the use of bent circular fibers, into which a fluor with appropriate wavelengths of absorption and emission is incorporated, which are imbedded in the tiles.[1] The many requirements for such waveshifting fluors have been detailed.[2] Organic fluors are used because their decay time is the fastest, and they can be disssolved in PS, which can be fabricated into large or intricate shapes. While the wavelength maxima of absorption and fluorescence of potential fluors can be calculated with fair accuracy,[3] fluorescence quantum yields (Φ_f) are not predictable. Radiation stability is related to photochemical stability and is hard to predict, but elements of $Z > 10$ can be avoided, as well as any functional group that is susceptible to free-radical reactions. Brightness is the product of Φ_f and the molar extinction coefficient (ϵ).[2] The desirable fast response times, called short fluorescence decay times (τ_f), have been inversely correlated with ϵ for ultraviolet absorption in oligophenylenes;[4] however, the longest practical emission wavelength obtainable from an oligophenylene, 390 nm, is from a sexiphenyl with no auxofluors (auxo-

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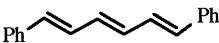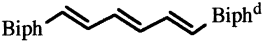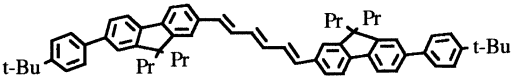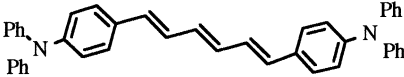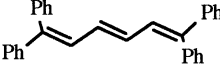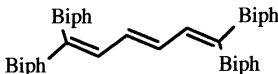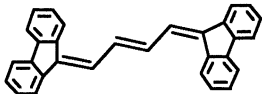
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TABLE 1. Optical Properties of (E)-1,6-Diaryl- and (E)-1,1,6,6-Tetraryl-1,3,5-hexatrienes in Toluene

Cpd.	Structure	UV-vis: λ_{max} nm (ε)	Fl Em: λ_{max} nm (RI)[b]	$\phi_f{}^c$
24a[a]	Ph⌒⌒⌒Ph	337 (60,000) 353 (81,000) 374 (56,000)	391 (44) 426 (88) 452 (100) 475 (80)	0.66
b	Biph⌒⌒⌒Biph[d]	368 (78,500) 387 (95,000) 407 (67,400)	432 (85) 455 (100)	1.00
c	(structure)	397 (90,000) 419 (110,000) 444 (85,000)	460 (98) 488 (100)	0.75
d	Ph₂N–C₆H₄–⌒⌒⌒–C₆H₄–NPh₂	423 (88,000) 445 (70,000)	470	0.82
26a	(tetraphenyl structure)	354 (53,000)	450	≈0.5
b	(tetrabiphenyl structure)	404 (40,700)	490	0.69
c	(difluorenylidene structure)	415 (63,600) 442 (103,800) 472 (102,100)	-	0.0

[a] From ref 4. [b] Fluorescence emission, RI = relative intensity. [c] Vs 9,10-diphenylanthracene at ϕ_f = 0.82 from refs 5 and 50. [d] 4-Biphenylyl.

chromes on fluors).[5] Carbon bridging of some of the rings as in an oligofluorene extends this wavelength only to about 437 nm.[5] A recent report on fluors which are agglomerations of benzoxazoles (or benzothiazoles) and phenylene groups gave fast fluors, but their solubilities and Stokes' shifts were too low.[6] Our attempt to use benzofuran-terminated oligofurans failed because these materials had too much self-absorption and were only moderately stable.[7] While the τ_f for 1,6-diphenyl-1,3,5-hexatriene (12 ns) is much too slow,[4] its wavelengths were promising (Table 1); thus we thought that incorporation of auxofluors might bathochromically shift the wavelengths into the range desired, which are absorption at 410 ± 10 nm and fluorescence emission at 480 ± 20 nm (blue-green), the difference being called the Stokes' shift, and that these might serve as model compounds. With τ_f = 1.1 ns a 1,4-distyrylbenzene (BPSB, Table 2) also seemed to be a promising fluorophore, but with even more bathochromic shift required. It is easier to obtain the large Stokes' shifts desired in a fluor with an electron-releasing auxofluor at one end and an electron-accepting auxofluor at the other ("push–pull auxofluors"); however, fluors with symmetrical auxofluors tend to have higher Φ_f and ϵ, and thus shorter τ_f, but at the cost of less Stokes' shift and poorer solubility.[5]

The dialkylamino group as an electron-releasing auxofluor provides the most extreme bathochromic shift of the common groups.[8] The magnitude of the shift is inversely proportional to the Hammett σ constant, this being most pronounced for the 9-julolidinyl group (see **31g**) with σ = −1.7.[9] The dialkylamino group is photochemically unstable on oligophenylenes,[10] but is stable on coumarins[11,12] and rhodamines[13] which absorb and emit at longer wavelengths. We now report our findings on 2,5-diphenyloxazoles, 1,3,5-hexatrienes, and 1,4-distyrylbenzenes, many bearing dialkylamino groups as auxofluors. On finding that such fluors were unstable, we switched to diarylamino groups based on a report on a benzothiazole analogue of fluor **7**;[14] these groups gave better overall photochemical stability on all three fluor types, and this finding then was applied to novel 2,7-distyrylfluorenes.

During the course of this work reports appeared on other photophysical properties of fluors **31d**[15,16] and

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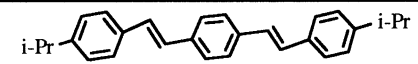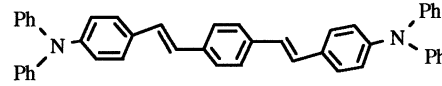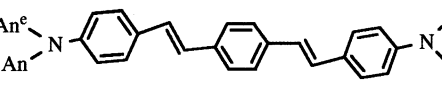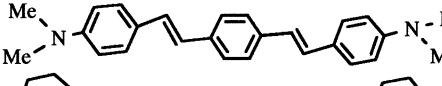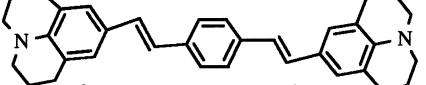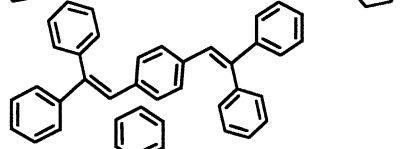
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TABLE 2. Optical Properties of (*E*)-1,4-Distyryl- and (*E*)-1,4-Bis(2-phenylstyryl)benzenes in Toluene

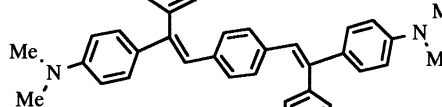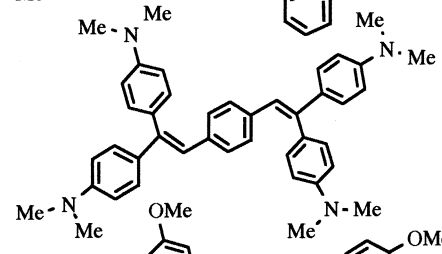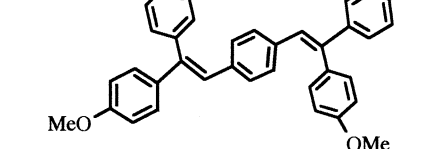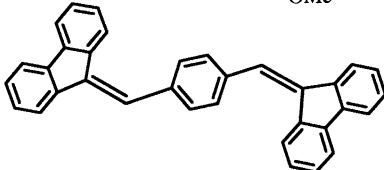| Cpd.	Structure	UV-vis: λ_{max} nm (ε)	Fl Em (RI)[b]: λ_{max} nm	ϕ_f[c]	RPS[d]
BPSB[a]	i-Pr···i-Pr distyrylbenzene	358 (71,000)	393 (78), 415 (100) 440 (58), 465 (100) 495 (100)	0.77	—
31d	Ph$_2$N···NPh$_2$	412 (70,000)	530 (46) 480 (100)	0.91[f]	7
e	An$_2$N···NAn$_2$[e]	420 (72,000)	512 (90) 555 (40)	0.74	7
f	Me$_2$N···NMe$_2$	408 (52,000)	447(100) 475 (70)	0.98	0.1
g	julolidyl derivative	420 (70,000)	467 (100) 498 (73)	0.87	0.01
32a	tetraphenyl derivative	354 (53,900)	550	0.01	—
b	Me$_2$N, Ph derivative	393 (39,600)	—	0.0	—
c	Me$_2$N (tetrakis) derivative	405 (21,200)	—	0.0	—
d	OMe (tetrakis) derivative	370 (47,700)	—	0.0	—
e	bis(fluorenylidene) derivative	368 (23,300)	—	0.0	—

[a] From ref 4. [b] Fluorescence emission, RI = relative intensity. [c] Vs 9,10-diphenylanthracene at ϕ_f = 0.82 from refs 5 and 50. [d] Relative photochemical stability, see text. [e] 4-Methoxyphenyl. [f] Lit. 0.85 from ref 15.

31f[16,17] or their homologues , which are of interest as laser dyes, two-photon absorbers, components of electroluminescent flat panel displays, and light-emitting diodes. Now there is keen interest in scintillation detection of γ rays and neutrons for homeland security using PS scintillators with dissolved fluors and waveshifters.

Known and reliable synthetic methods were deliberately selected; nevetheless, we were able to simplify some

reported procedures for Buchwald-type *N*-arylations, and to improve the Emmons−Horner reaction.

Discussion and Results of Syntheses

For fluor **7** (Scheme 1) the reported nitration of fluorene **1**[18] was improved to give nitrofluorene **2**, in which the iodo group was then replaced with cyano in 91% yield to give **3**. Basic hydrolysis failed, but acid hydrolysis utilizing propanoic acid as a cosolvent gave

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SCHEME 1. Synthesis of 2-(6-Methyl-2-benzoxazolyl)-7-[bis(4-methoxyphenyl)amino]-9,9-dipropylfluorene
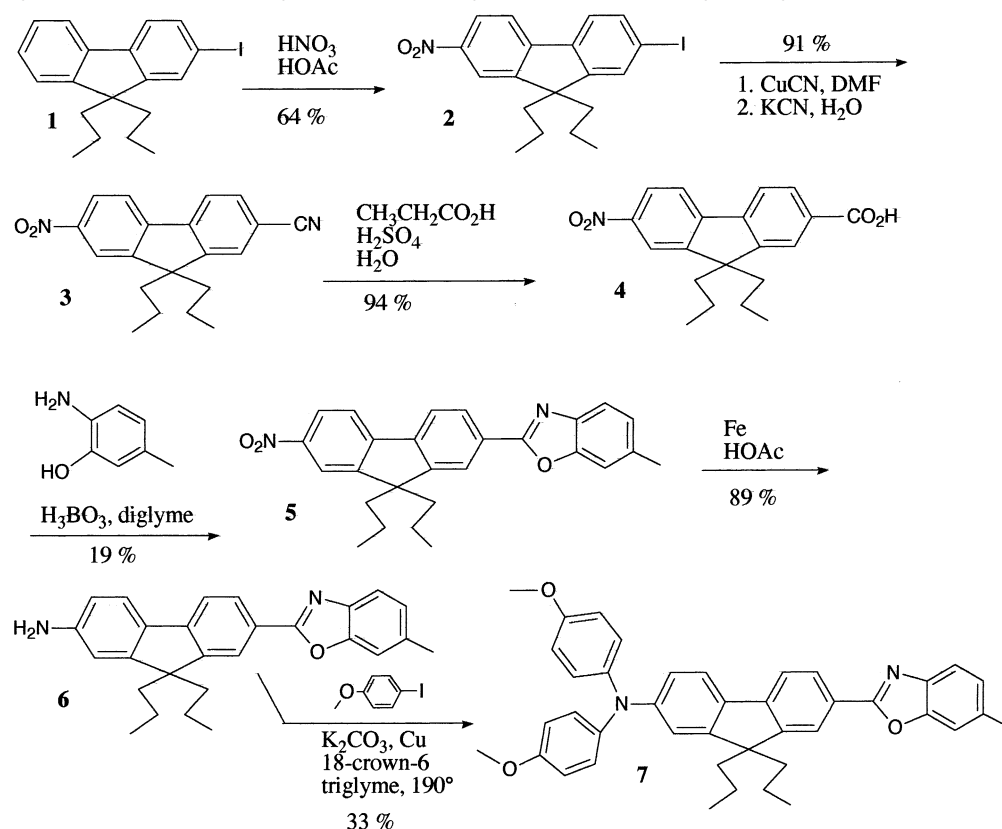
acid **4** in excellent yield. Formation of oxazole **5** in a 1-pot reaction gave much lower yields than we obtained when the intermediate amide was isolated in syntheses of related fluors;[19] we avoided the use of polyphosphoric acid for this condensation because of the extreme insolubility of **4** in it. Reduction of the nitro group in **5** by means of iron in acetic acid gave 89% of aminofluorene **6**. Diarylation to form **7** was carried out according to Belfield[14] using triglyme as solvent rather than 1,2-dichlorobenzene.

For fluor **14** (Scheme 2) we worked out a convenient di-*N*-ethylation of 4′-aminoacetophenone **8** with diethyl sulfate in dioxane with use of diisopropylethylamine as the acid acceptor. The formation of the ammonium salt of **9** allowed regiospecific bromination to give the phenacyl bromide **10**, isolated as an oily free base. A Gabriel synthesis was preferable to the Délèpine reaction because the diammonium salt **13** has the same solubility as ammonium bromide, whose presence was avoided, while the phthalic acid byproduct was easily removed from **13** with acetone. A 1-pot oxazole formation (not optimized) gave **14**.

For fluor **20** (Scheme 3), oxazole **18** was an obvious intermediate target, since the cyano group is compatible with Buchwald conditions, so 2,4′-dibromoacetophenone **15** was converted via the Délèpine reaction to the phenacylammonium salt **16**, which was amenable to recrystallization from water, thus giving a complete separation from ammonium bromide in this case; then a 1-pot oxazole formation gave **18**. The known bis(4-

methoxyphenyl)amine **19**[20] was prepared by Buchwald conditions in which expensive resolved BINAP (the *racemic* not being available at the time) was advantageously replaced by dppf,[21] and the workup was simplified. A second buchwald Reaction, this time between **18** and **19**, gave **20** in good yield.

A simple Vilsmeier reaction on triphenylamine had been reported to give the aldehyde **23d** (Scheme 4) in unreported yield after a difficult fractional crystallization;[22] we worked out a method to yield 85% after a single recrystallization from ethanol, obviating the need for the multistep method of Tew et al.[21] A Buchwald amination of 4-bromobenzonitrile with **19** gave triarylamine **27** in good yield (Scheme 5). This was converted to the aldehyde **23e** in the manner of Tew et al.[21] with some modification of conditions.

The known phosphonate esters **22** (Scheme 4) and **30** (Scheme 5) were prepared by either improved or simplified methods. The bis(chloromethyl)fluorene **38** (Scheme 6) had been reported by chloromethylation of 9,9-dipropylfluorene;[18] knowing how tedious this had been, we took advantage of the availability of a number of fluorene derivatives to develop an alternate route. First the dicarboxylic acid **33** was esterified to form **34**, but the reduction with sodium bis(2-methoxyethoxy)aluminum hydride in toluene, while destroying all carbonyl groups,

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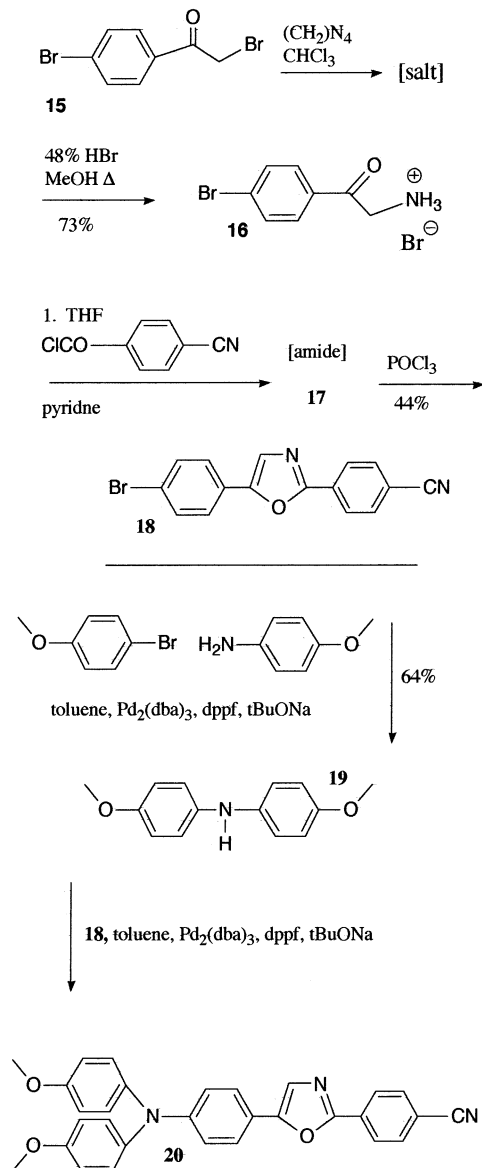(21) Tew, G. N.; Pralle, M. U.; Stupp, S. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 517.

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SCHEME 2.   Synthesis of 2-(4-Cyanophenyl)-5-[4-(diethylamino)phenyl]oxazole

SCHEME 3.   Synthesis of 2-(4-Cyanophenyl)-5-{4-[bis(4-methoxyphenyl)amino]phenyl}oxazole
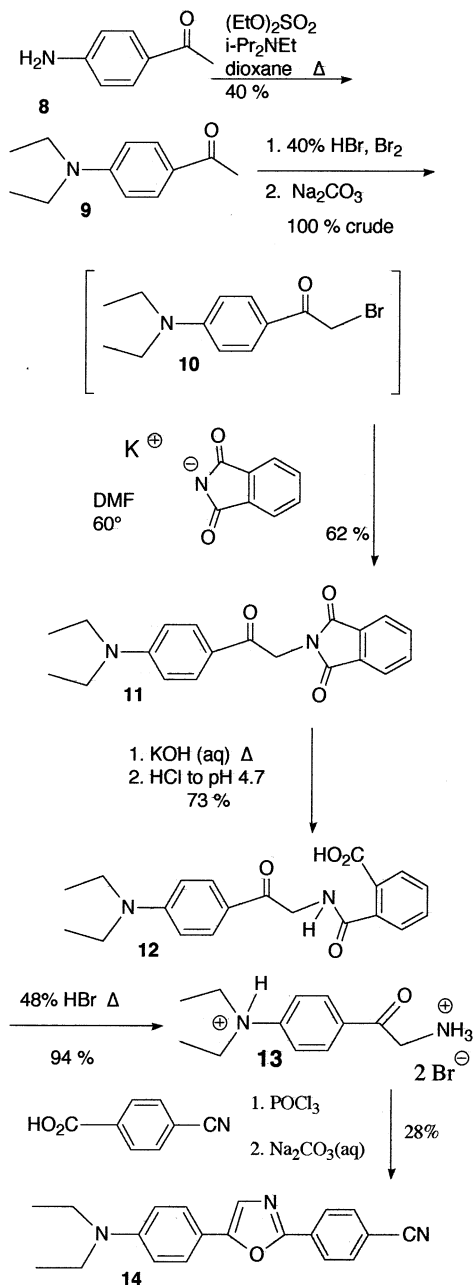
did not give a purifiable diol (**35**). The di-Grignard reagent of 2,7-dibromo-9,9-dipropylfluorene **36** gave liquid dialdehyde **37**, whose reduction with sodium bis(2-methoxyethoxy)aluminum hydride then gave clean diol **35**. An easy 3-phase reaction with 12 M hydrochloric acid and toluene gave **38**, which was converted to crystalline phosphonate ester **39** by an Arbuzov reaction.

The 1,3,5-hexatrienes **24a**–**d** (Scheme 4), the 1,4-distyrylbenzenes **31d**–**g** and **32a**–**e** (Scheme 5), and the 2,7-distyrylfluorenes **40a,d,e** (Scheme 6) were all prepared by a version of the Emmons–Horner reaction that favors all *(E)* alkenes (except for **26a**–**c** and **32a**–**e**); this involves the use of DMF as solvent and, in our version, potassium *tert*-butoxide as the base. Many permutations of reagent addition have been reported. With these, when sodium methoxide is the base, yields of crude alkenes are

typically 50–70%. We found that DMF will dissolve potassium *tert*-butoxide at 7 mL/g, and that the solution may be added to the diphosphonate and carbonyl compound in a controlled manner so that the transitory formation of the red carbanion may be observed. This "indicator" showed that up to almost a 2-fold excess of potassium *tert*-butoxide increased yields of crude alkenes to 80–100% in several cases when benzaldehydes were used, but such yields were not obtained when benzophenones were used. Procedures for a number of alkenes previously reported in the nonpatent literature are included when our method of synthesis was different, or no optical spectra were found, or where no NMR or no high-field NMR data were found.

Discussion and Results of Photophysical Properties

Belfield et al. had not given the absorption and fluorescence maxima in toluene, which is of similar

SCHEME 4.   Syntheses of 1,6-Diaryl- and 1,1,6,6-Tetraaryl-1,3,5-hexatrienes
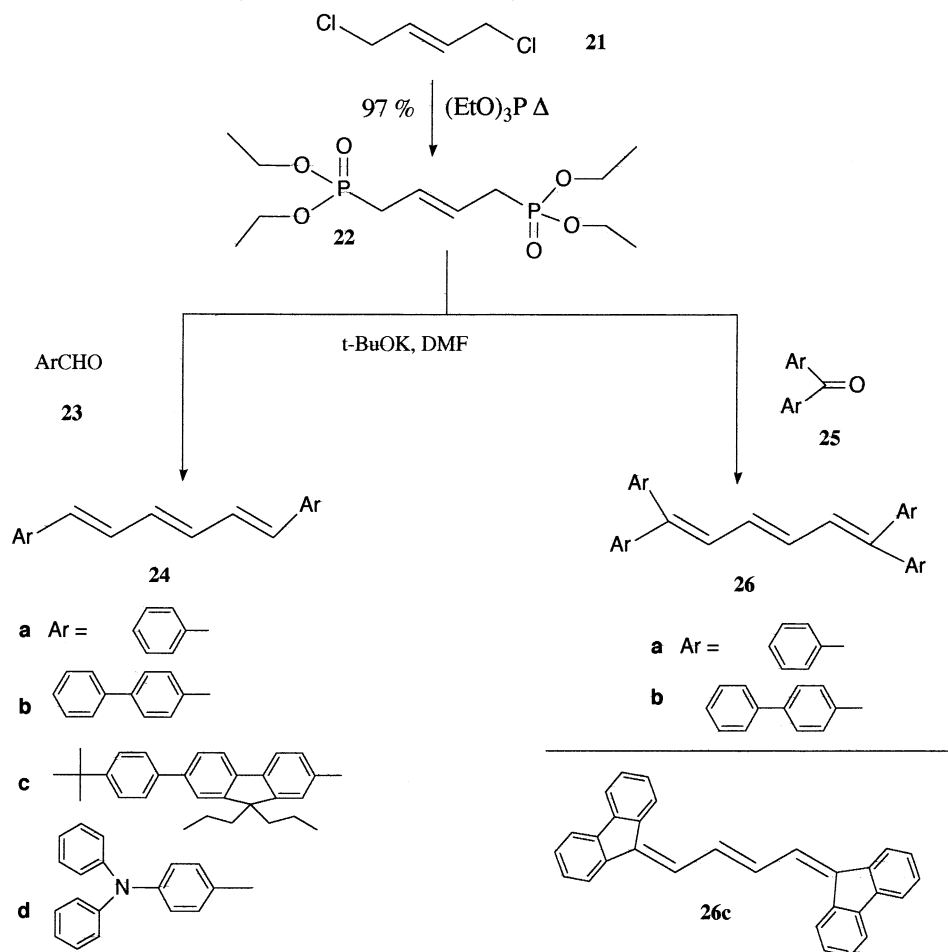
polarity to PS, for a benzothiazole analogue of fluor **7**; they used THF as the solvent, which bathochromically shifts the wavelengths of such solvatochromic fluors bearing push−pull auxofluors. Also the Φ_f, ϵ, and τ_f values were not given.[14] We found that the absorption max of **7** at 401 nm (ϵ = 48 700) and the Φ_f = 0.86 were acceptable; but its emission max at 455 nm was too short for our purposes (all determined in toluene), and the τ_f = 4.55 ns was too slow in PS.

Earlier work on 2,5-diphenyloxazoles, including some with dialkylamino groups, showed that they were efficient fluors with large Stokes' shifts.[23] Cyano group(s) on terphenyl gave improved scintillation fluors,[24] so we decided to combine these two types of groups as push−pull auxofluors as in fluor **14**. The 80-nm Stokes' shift was excellent (Figure 1), along with a good Φ_f of 0.69; but the absorption max was too short at 394 nm, and the low ϵ of 27 000 would have led to a slow τ_f.[2] Determination of the radiation damage to fluors in PS using γ rays is a slow and involved process, which will be reported separately for **7**, **31d,e**, and **40d,e**. We were able to glean the relative photochemical stabilities (RPS) of fluors by exposing 1−3 × 10^{-5} M solutions of them in toluene to diffuse daylight and fluorescent light on a

diurnal basis, and noting the time for the fluorescence to fade. Fluor **14** faded noticeably in 2 weeks and completely in 5 weeks, a poor performance.

So the diaryl analogue **20** made use of 4-methoxyphenyl instead of ethyl groups and **20** showed a 103-nm Stokes shift, from 402 nm (ϵ = 29 100) to 505 nm with Φ_f of 0.63, and did not fade for at least 5 weeks. The low ϵ would indicate low brightness as well as a slow τ_f;[2] the former is obvious to the naked eye vs the distyrylbenzene **31e**, for example, which had ϵ = 72 000 and about the same Φ_f 0.74.

In the 1,6-diaryl-1,3,5-hexatrienes (Table 1) extension of conjugation by substitution of phenyl (**24a**) by 4-biphenylyl (**24b**) gave higher ϵ but not much bathochromic shift. The 2-phenylfluorenyl group (**24c**) gave still higher ϵ and about 33 nm of bathochromic shift, but the *effective* Stokes' shift (444 to 460 nm) was inadequate. The diphenylamino group (**24d**) displayed a larger Stokes' shift (445 to 470 nm), had high ϵ, and was as stable as **24b**, each with an RPS of 5 months. The loss of fluorescence was probably governed by the rate of E/Z isomerization.[25] The 1,1,6,6-tetraaryl-1,3,5-hexatrienes **26a,b** had lower ϵ but high Φ_f, 0.69 for **26b**; thus **26b** is being further tested for our purposes, partially because of its ideal wavelengths (Figure 2). The fluorenylidenebutene **26c** had high ϵ, but Φ_f = 0.

(23) Ott, D. G.; Hayes, F. N.; Hansbury, E.; Kerr, V. N. *J. Am. Chem. Soc.* **1957**, *79*, 5448.
(24) Velázquez, C.; Castrillón, J. *Intl. J. Appl. Radiat. Isotopes* **1974**, *26*, 237.

(25) Magoon, E. F.; Zechmeister, L. *J. Am. Chem. Soc.* **1955**, *77*, 5642.

SCHEME 5. Syntheses of 1,4-Distyrylbenzenes
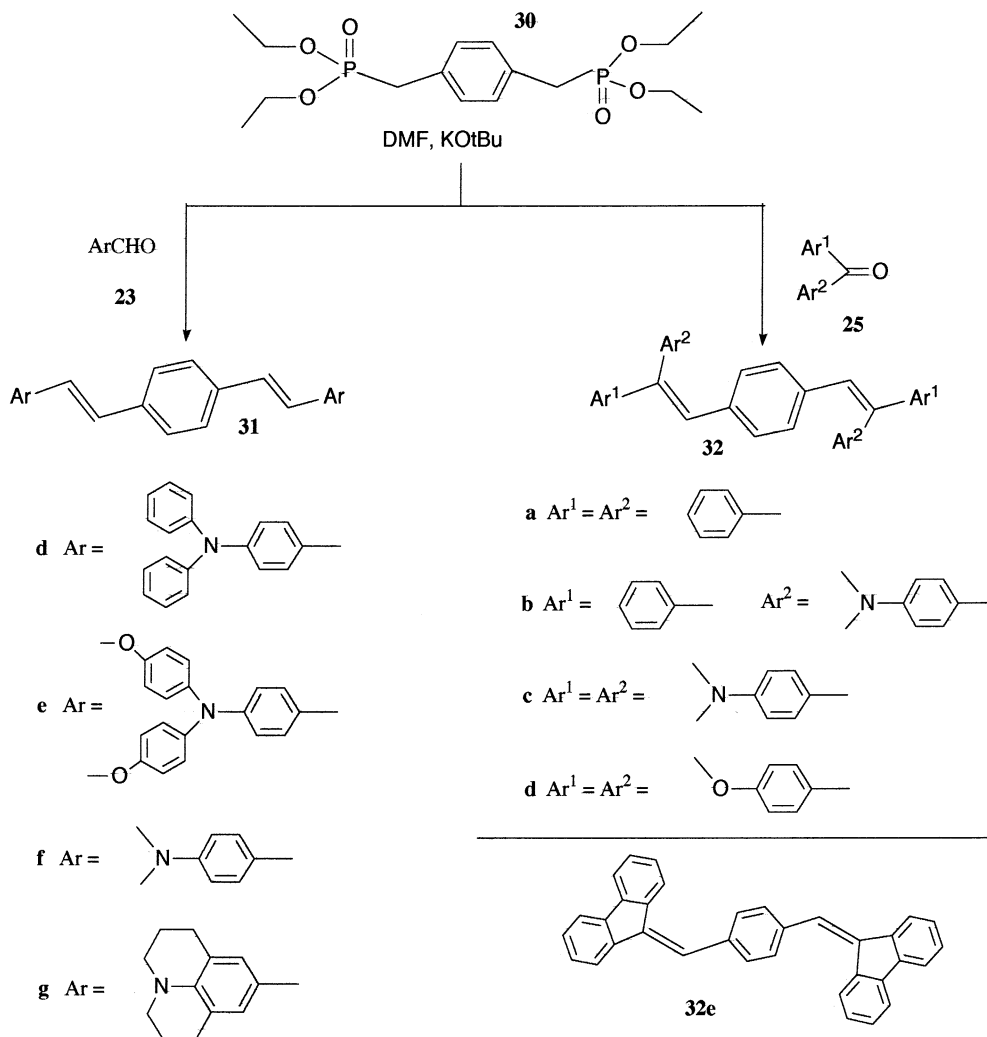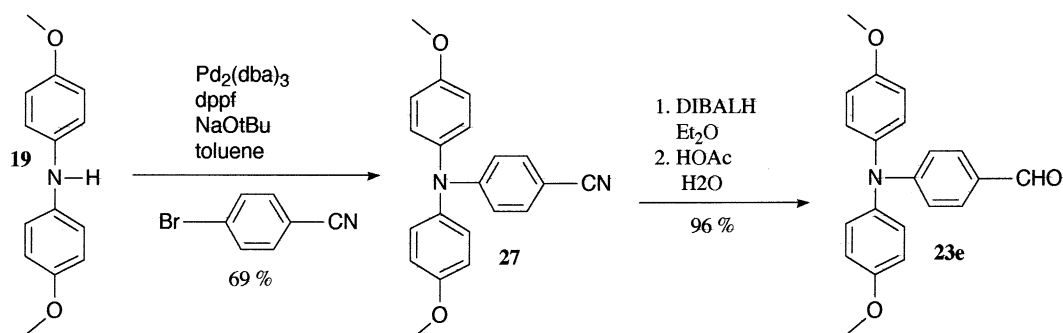
The excellent properties of 1,4-distyrylbenzene "BPSB" (Table 2), which included a τ_f of 1.1 ns,[4] inspired our extensive efforts to bathochromically shift its wavelengths by about 70 nm. The earliest derivatives we prepared were the dialkylaminos **31f,g**, whose photophysical properties we had reported;[26] these displayed both high ϵ and Φ_f, but **31f** had a very poor RPS of 0.1 month, so based on the findings for coumarins used as

laser dyes,[27,28] we thought that the julolidinyl analogue **31g** would be more stable; instead it had the poorest RPS of any fluor made in this project, ≈ 0.01 month. Next the 2,2-diarylethenyl derivatives **32a–e** were prepared, but these also showed low ϵ, apparently because of steric hindrance to coplanarity in the S_1 state; moreover all had $\Phi_f = 0$. Finally the diarylamino fluors **31d,e** were synthesized and found to have high Φ_f, high ϵ, and an

(26) Kauffman, J. M.; Bajwa, G. S.; Litak, P. T. In *SCIFI 97: Conference on Scintillating Fiber Detectors*, University of Notre Dame, Nov 97; Bross, A. D., Ruchti, R. C., Wayne, M. R. Eds.; American Institute of Physics Conf. Proc. 450, Woodbury, NY, 1998; p 3.

(27) Fletcher, A. N.; Bliss, D. E.; Kauffman, J. M. *Opt. Commun.* **1983**, *47*, 57.
(28) Jones, G., II; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.

SCHEME 6.   Syntheses of 2,7-Distyrylfluorenes
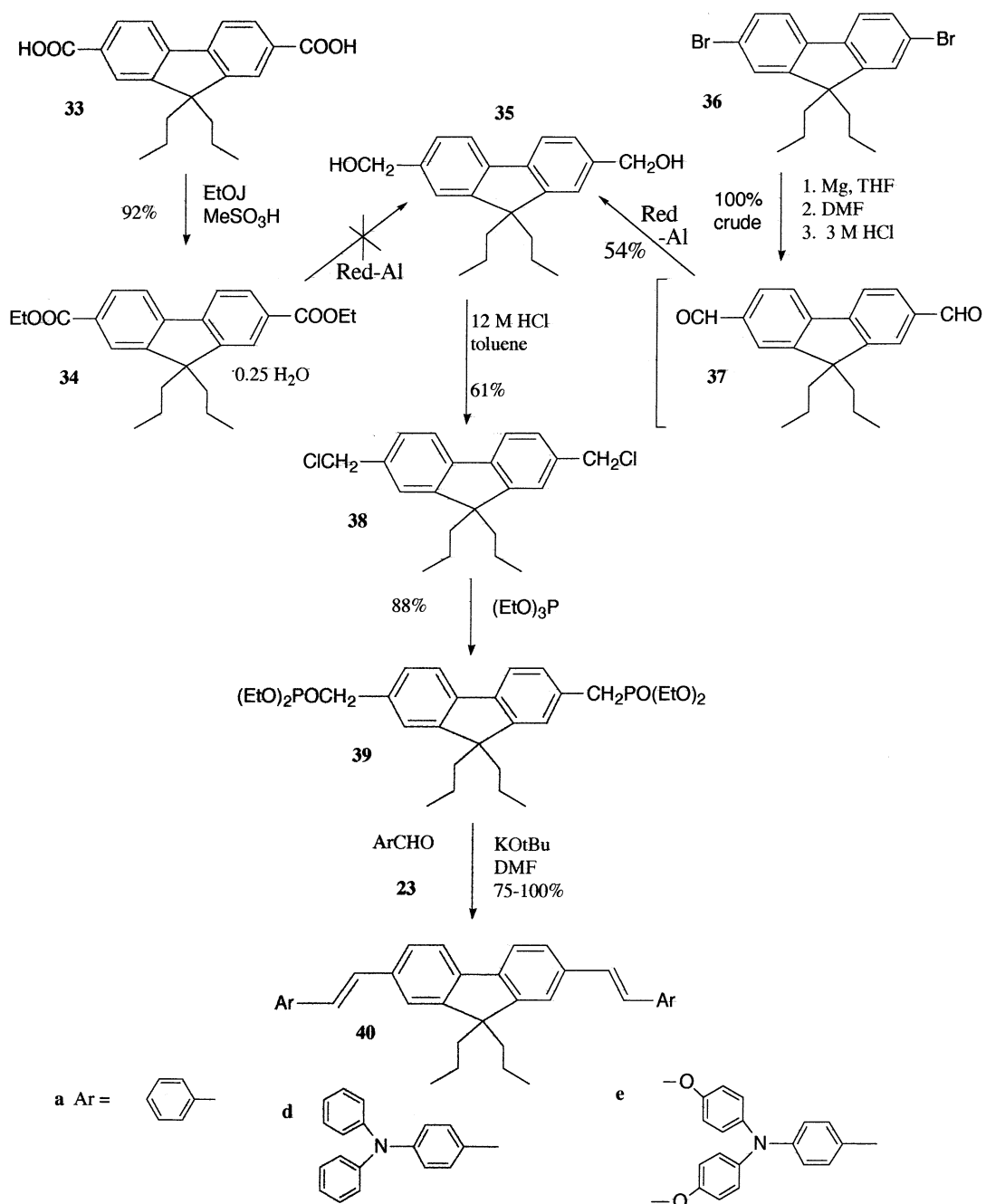
RPS = 7 months; these proved to have the best combination of properties for our purposes (see Figures 3 and 4), including τ_f = 1.86 (**31d**) and 2.25 ns (**31e**).

As a model compound the fluorene **40a**[18] (Table 3) proved to have a smaller Stokes' shift and very little bathochromic shift compared with BPSB, but the increase in ϵ was substantial and indicated likely benefits in brightness and τ_f. Accordingly, fluors **40d,e** were synthesized (Figures 5 and 6), which display τ_f = 1.73 (**40d**) and τ_f = 2.05 ns (**40e**), the fastest green-emitting fluors of which we are aware, but not as photostable as the corresponding distyrylbenzenes (RPS = 6 and 4.5 months respectively).
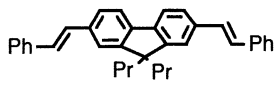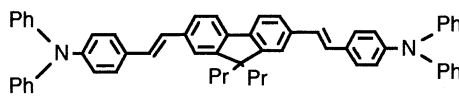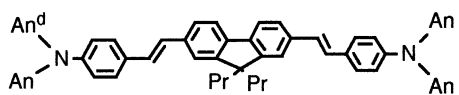
Wavelengths of absorption and fluorescence had been calculated for **24a–c**, **26a–c**, and **32a**;[3] the accuracy varied from excellent to fair and Φ_f was not predictable. For example, the predicted absorption maximum for **24c** was 382 nm vs actual triple maxima of 397, 419, and 444 nm, while the predicted emission maxima were 461, 488, and 521 nm vs actual maxima of 460 and 488 nm. The calculated absorption maximum for **26c** was 392 nm vs actual maxima of 415, 442, and 472 nm; while the predicted emission max was 465 nm vs no emission. According to Walter M. F. Fabian, these calculations fail altogether when amino groups are present, and so they had not been done for any of the amino compounds.

Conclusions

The Buchwald and Emmons–Horner reactions were further developed for syntheses of di- and triarylamines

TABLE 3. Optical Properties of (*E*)-2,7-Distyrylfluorenes in Toluene

Cpd.	Structure	UV-vis: λ_{max} nm (ε)	Fl Em: λ_{max} nm (RI)[a]	ϕ_f[b]	RPS[c]
40a	Ph—=—[fluorene, Pr Pr]—=—Ph	369 (91,000) 386 (71,000)	405 (95), 427 (100) 451 (45), 490 (15)	High	—
d	Ph,Ph-N—C6H4—=—[fluorene, Pr Pr]—=—C6H4—N-Ph,Ph	407 (97,000) 425 (83,000)	456 (100), 487 (85) 530 (45)	0.91	6
e	An[d],An-N—C6H4—=—[fluorene, Pr Pr]—=—C6H4—N-An,An	416 (99,000) 440 (90,000)	472 (100), 500 (86) 540 (38)	0.89	4.5

[a] Fluorescence emission, RI = relative intensity. [b] Vs 9,10-diphenylanthracene at ϕ_f = 0.82 from refs 5 and 50. [c] Relative photochemical stability, see text. [d] 4-Methoxyphenyl.
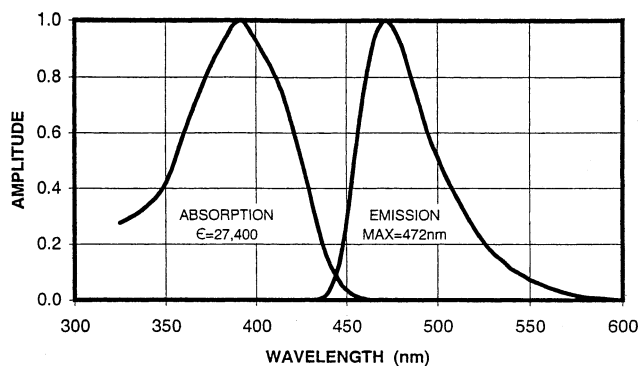

FIGURE 1. UV−vis and emission spectra of 5-(4-diethylaminophenyl)-2-(4-cyanophenyl)oxazole (**14**).
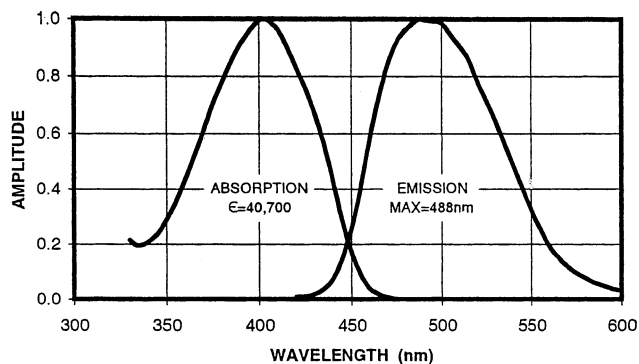

FIGURE 2. UV−vis and emission spectra of 1,1,6,6-tetra-4-biphenylyl-1,3,5-hexatriene (**26b**).

FIGURE 3. UV−vis and emission spectra of 1,4-bis[4′-(diphenylamino)styryl]benzene (**31d**).
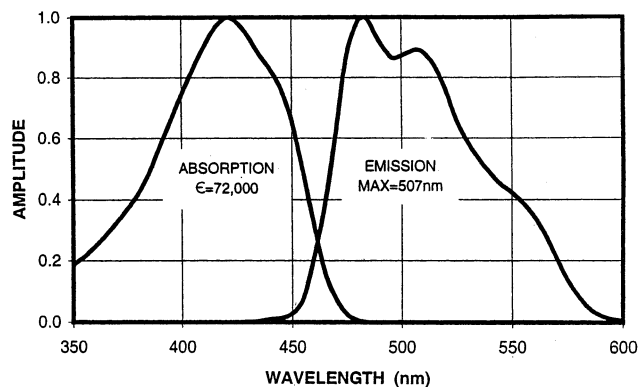
FIGURE 4. UV−vis and emission spectra of **1,4**-bis[4′-bis(4-methoxyphenyl)aminostyryl]benzene (**31e**).

and alkenes, respectively. The former is clearly superior to Ullmann *N*-amination even with use of a phase-transfer catalyst. The latter was improved by a novel order of reagent addition and the use of excess base. A 2-benzoxazolyl-7-(4-diphenylamino)phenylfluorene (**7**) was bright, but had an emission wavelength too short for this project, and was too slow. Fluors bearing diarylamino groups were more photochemically stable than those with dialkylamino groups: compare 2-(cyanophenyl)-5-(4-aminophenyl)oxazoles **14** and **20**. This was true also in 1,4-bis(4′-aminostyryl)benzenes: compare **31d,e** with **31f,g**. The 1,6-diaryl-1,3,5-hexatrienes **24a−d** showed higher ε and Φ_f than the 1,1,6,6-tetraaryl-1,3,5-hexatrienes **26a−c**. The 1,4-distyrylbenzenes **31d−g** similarly showed higher ε and Φ_f than the 1,4-(2-phenylstyryl)benzenes

32a−e. The 2,7-distyrylfluorenes **40a,d,e** had higher ε and Φ_f than the 1,4-distyrylbenzenes **31d−g** and were in fact visibly brighter and slightly faster. Thus several new compounds were prepared that were promising as waveshifting fluors for PS fibers, which would serve as a key component of scintillation detectors of high-energy particles from accelerators.

Experimental Section

General Methods. General procedures have been previously described.[29] Air-sensitive reactions were conducted under argon. Dibutyl Carbitol (DBC) was diethylene glycol dibutyl ether, Aldrich 20,562-1. The potassium *tert*-butoxide (KOtBu)

FIGURE 5. UV–vis and emission spectra of 1,4-bis[4′-bis-(diphenylamino)styryl]-9,9-dipropylfluorene (**40d**).

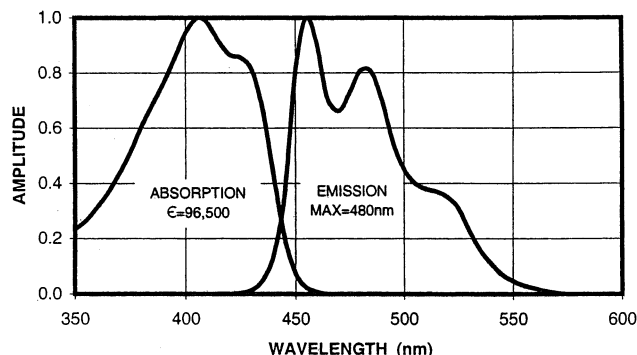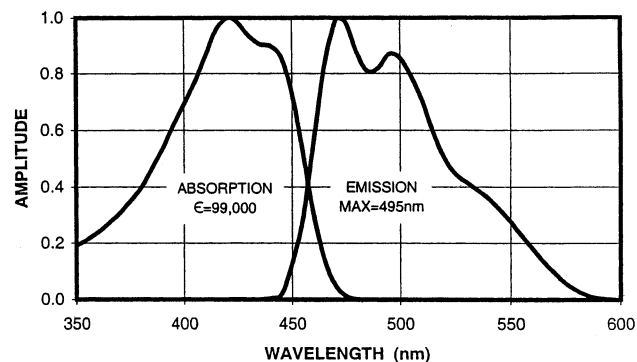**FIGURE 6.** UV–vis and emission spectra of 1,4-bis[4′-bis(4-methoxyphenyl)aminostyryl]-9,9-dipropylfluorene (**40e**).

was from Callery Chemical Co. Division of MSA, Inc. Solvents used in moisture-sensitive reactions were dried over 3A Molecular Sieve. All other solvents and reagents not given citations were used as received from common commercial sources; uncommon sources are named. Preparation of the catalyst palladium(II) chloride 1,4-bis(diphenylphosphino)-butane (PdCl$_2$·dppb) has been described.[30] Florisil was Aldrich 22,074-4. Next to mp, pc means phase-change. Elemental Assays were performed by Micro-Analysis, Inc., of Wilmington, DE. For AA′XX′ spin systems (i.e., 4-substituted phenyl rings) in ^{1}H NMR spectra, only the $^3J_{HH}$ coupling is reported. All UV and fluorescence emission spectra were determined on $1-3 \times 10^{-5}$ M solutions in toluene. Corrected emission wavelengths were found with a Farrand Mk. I spectrofluorimeter rebuilt by Optical Technology Devices, Inc., or a Varian Cary Eclipse; the latter was used to measure the Φ_f values on the solutions used for UV spectra as described previously, using 9,10-diphenylanthracene (Polysciences, Inc.) in toluene as a reference with $\Phi_f = 0.82$.[5] The fluorescence decay times (τ_f) were determined by means of front-face laser excitation of a solution of the sample where the reciprocal of the log of emission intensity vs time of the first linear section of the curve is used. A Photon Technology International (PTI) GL-3300 Nitrogen Laser with a tunable PTI photometer was interfaced with a Windows NT PC operating the PTI TimeMaster Fluorescence Lifetime software. The laser is fired into the face of the sample and the photometer records the intensity emitted at right angles to the laser beam at the wavelength determined separately on a Hitachi spectrofluorimeter. The photometer is stepped though a selected timing range and the intensity is recorded. The laser is fired 5 to 10 times at each time delay from the clock start, usually in steps of $0.1-0.3$ ns. The light

(29) Kauffman, J. M.; Khalaj, A.; Litak, P. T.; Bajwa, G. S.; Novinski, J. A. *J. Heterocycl. Chem.* **1994**, *31*, 957.
(30) Kelley, C. J.; Ansu, K.; Budisusetyo, W.; Ghiorghis A.; Qin, Y.; Kauffman, J. M. *J. Heterocycl. Chem.* **2001**, *38*, 11.

received is averaged over the number of laser firings for each clock delay, and these means are recorded to a text file of delay times and intensities; then these files are transferred to another computer for analysis with MS Excel, by which the log of the intensity is plotted against the delay time, in which 2 linear portions of each curve are normally found. The τ_f is the reciprocal of the slope of the first linear portion of each curve.

Synthesis of 9,9-Dipropyl-2-iodo-7-nitrofluorene (2). A mixture of 9,9-dipropyl-2-iodofluorene[18] (**1**, 37.6 g, 0.1 mol), 300 mL of acetic acid, and 20 mL of 90% nitric acid was heated slowly to reflux, which was maintained for 4 h. The mixture turned dark, then light, and was allowed to cool to 20 °C before being quenched in 1.2 L of water with propeller stirring. The crude product was collected, washed with 700 mL of water and a minimum of 50% methanol, dried at 60 °C/20 Torr/3 h to give 45.4 g of crude **2**. This was recrystallized from 300 mL of 2-propanol at −2 °C, decanted, and the damp solid recrystallized from 250 mL of hexane at −2 °C to give huge yellow prisms, mp 117−120 °C, 27.2 g (64%) (lit.[18] 46%, mp 121−122 °C).

Synthesis of 2-Cyano-9,9-dipropyl-7-nitrofluorene (3). A suspension of 9,9-dipropyl-2-iodo-7-nitrofluorene (**2**, 50.0 g, 0.119 mol), copper(I) cyanide (12.75 g, 0.142 mol), and 85 mL DMF was boiled under reflux overnight and allowed to cool to about 50 °C, then poured into a solution of potassium cyanide (29.4 g, 2.21 mol) in 210 mL of water with propeller stirring. During the course of an hour the gummy solid turned hard and was collected, washed with 100 mL of water, ground in a mortar, slurried with 300 mL of 47.5% ethanol, re-filtered, washed on the filter with 300 mL of 47.5% ethanol, and then dried at 80 °C/25 Torr/2 h to give 42.3 g. This was extracted from a glass thimble in a large Soxhlet with 600 mL of cyclohexane and the extract was transferred to a beaker, diluted with 250 mL of hexane, and allowed to stand at 20 °C overnight to yield nice tan spars, mp 161−161.5 °C, 36.7 g (97%). Anal. Calcd for C$_{20}$H$_{20}$N$_2$O$_2$: C, 74.98; H, 6.29; N, 8.75. Found: C, 74.70; H, 6.30; N, 8.69. ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.69 (10H, m), 2.07 (4H, m), 7.80 (4H, m), 8.29 (1H, s), 8.33 (1H, dd, $J = 2.2$, $J = 8.2$).

Synthesis of 9,9-Dipropyl-7-nitrofluorene-2-carboxylic Acid (4). A mixture of 2-cyano-9,9-dipropyl-7-nitrofluorene (**3**, 36.7 g, 0.115 mol) and 73.4 mL each of acetic acid, water, and sulfuric acid was boiled under reflux for 2 days, allowed to cool below 100 °C, and diluted with 425 mL of water; this mixture was cooled in a water bath to 20 °C, and the product was collected, washed with 700 mL of water, and air-dried for 2 days to give 36.6 g (94%), mp 255−265 °C. IR (CHCl$_3$, cm^{-1}) 3400−2800 (v br, OH), 3015 (ArCH), 2980, 2930, 2872 (alCH), 1685 (C=O), 1518, 1348 (NO$_2$), 1220, 1200 (C−O), 640 (ArCH).

The product of another earlier run, after recrystallization of 0.4 g from 10 mL of 2-methoxyethanol with 4 mL of water, gave pale yellow transparent spars, mp s. 245, 256−265 °C. Anal. Calcd for C$_{20}$H$_{21}$NO$_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.90; H, 6.20; N, 4.40.

Synthesis of 9,9-Dipropyl-2-(6-methyl-2-benzoxazolyl)-7-nitrofluorene (5). A mixture of 9,9-dipropyl-7-nitrofluorene-2-carboxylic acid (**4**, 6.20 g, 0.0813 mol), 6-amino-*m*-cresol (2.25 g, 0.0813 mol), boric acid (1.13 g, 0.0813 mol), and 110 mL of diglyme was boiled under reflux so as to extract 20 g of indicating 4A Mol Sieve in a small Soxhlet for 20 h. At 20 °C the mixture was poured into 300 mL of water and 50 mL of 95% ethanol. A tarry material separated. This was extracted with 100 mL, then 50 mL of chloroform; the extracts were washed with 300 mL of water and dried with 20 g of calcium chloride for 1 h. The supernatant was poured through a 4 × 10 cm column of neutral alumina (Aldrich 19,997-4) followed by 350 mL of chloroform. The eluate was evaporated to deposit 2.5 g of orange oil which crystallized well from 12.5 mL of abs ethanol. The orange prisms were collected, washed with methanol, and air-dried to give 1.49 g (19%), mp 175−177 °C.

Anal. Calcd for $C_{27}H_{26}N_2O_3$: C, 76.03; H, 6.14; N, 6.57. Found: C, 75.77; H, 5.90; N, 6.53.

Synthesis of 7-[Bis(4-methoxyphenyl)amino]-9,9-dipropyl-2-(6-methyl-2-benzoxazolyl)fluorene (7). A suspension of 9,9-dipropyl-2-(6-methyl-2-benzoxazolyl)-7-nitrofluorene (**5**, 1.41 g, 0.00331 mol), 1.9 g of iron powder (Lancaster 13237), and 40 mL of acetic acid was heated to boiling. The heat was turned off, and when boiling ceased, 0.39 g of iron (0.0231 mol in all) was added. This mixture was boiled under reflux for 10 min, then was allowed to cool. The supernatant was decanted into 80 mL of water, this mixture was stirred 1 h, and the **7-amino-9,9-dipropyl-2-(6-methyl-2-benzoxazolyl)fluorene (6)** was collected, washed with 50 mL of 50% methanol, and dried at 110 °C/20 Torr/1 h to give 3.23 g, mp s. 192, 230–251 °C. This product was recrystallized from a mixture of 30 mL of 2-methoxyethanol and 10 mL of water to give 1.17 g (89% crude), mp pc 203 °C, pc 236–246, 247–253 °C. The product displayed a bright blue fluorescence under longwave UV in toluene.

This crude amine (**6**, 1.17 g, 0.00295 mol), 4-iodoanisole (3.00 g, 0.0118 mol), potassium carbonate (3.26 g, 0.0236 mol), copper powder (1.0 g), 18-crown-6 (0.26 g), and 13 mL of triglyme was heated to 192 °C for 29 h by controlling the heating with a Therm-O-Watch relay. The mixture was allowed to cool to ≈60 °C and poured into 60 mL of methanol, and the flask was rinsed with 10 mL of methanol, producing a nice granular solid, which was collected, washed with 50% methanol, and air-dried overnight to give 2.2 g with a second crop of 0.26 g. Combined, these were extracted from a small Soxhlet with 125 mL of heptane in 90 min, and the extract kept at −20 °C overnight to give material, after decantation and drying, of mp 149–151 °C. This product was recrystallized from 10 mL of 1-propanol at −2 °C overnight, then from a mixture of 20 mL each of abs ethanol and acetonitrile with 15 mL of heptane, decanting from some insoluble yellow stuff before cooling to −20 °C overnight, to yield 0.59 g (33%) of **7**, mp 196.5–198.5 °C. Anal. Calcd for $C_{41}H_{40}N_2O_3$: C, 80.89; H, 6.62; N, 4.60. Found: C, 81.14; H, 6.57; N, 4.50. ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.70 (10H, m), 1.86 (2H, m), 2.51 (3H, s), 3.82 (6H, s), 7.01 (12H, m), 7.54 (3H, m), 8.18 (2H, m). $\tau_f = 4.55$ ns.

Synthesis of 4′-(Diethylamino)acetophenone (9). A mixture of 4′-aminoacetophenone (**8**, 96.0 g, 0.710 mol), diethyl sulfate (204 mL, 241 g, 1.562 mol), diisopropylethylamine (273 mL, 202 g, 1.562 mol), and 700 mL of dioxane was boiled under reflux for 4 days, cooled to 20 °C in a water bath, and quenched in 700 mL each ice and water; the crude was collected, washed with 100 mL of water, then 100 mL of cold 25% methanol, and the tarry solid was taken up in 300 mL of dichloromethane; the solution was dried with 25 g of sodium sulfate and evaporated in a tared 500 mL Büchi flask to give 72 g of dark brown oil, which was distilled under vacuum using a spray trap. A single cut, bp 159–172 °C/0.25 Torr was taken to yield 58 g (43%), which solidified on keeping, mp 41.5–44.5 °C (lit.[31] mp 47–48 °C).

The product of an earlier run, mp 42–43.5 °C, was recrystallized from 32 mL of methanol and 10 mL of water at −20 °C to give material of mp 43–44.5 °C. ^{1}H NMR (60 MHz, CDCl$_3$) δ 1.20 (6H, t, $J = 8.0$), 2.48 (3H, s), 3.45 (4H, q, $J = 8.0$), 6.65 (2H, AA′XX′, $J = 9.0$), 7.90 (2H, AA′XX′, $J = 9.0$).

Synthesis of N-[4′-(Diethylamino)phenacyl]phthalimide (11). The 4′-(diethylamino)acetophenone (**9**, 43.9 g, 0.230 mol) was dissolved in 90 mL of 40% (yes, forty) hydrobromic acid and treated with a solution of bromine (11.8 mL, 36.8 g, 0.230 mol) in 56 mL of 40% hydrobromic acid over about 40 min, and the mixture was kept overnight at 20 °C, diluted with 225 mL of water, and neutralized with a slight excess of solid sodium bicarbonate, then extracted with 330 mL of chloroform. The extract was dried over sodium sulfate and evaporated with a bath temperature ≤20 °C to yield 83.5 g of crude 4′-(diethylamino)phenacyl bromide **10**.

(31) Nineham, A. W. *J. Chem. Soc.* **1952**, 635.

This was taken up in 215 mL of dry DMF, treated with potassium phthalimide (46.9 g, 0.253 mol), and held at 75 °C/18 h. The suspension was quenched in 900 mL of water with mechanical stirring, which was maintained for 40 min, and the product was collected, washed with 500 mL of water, then 50 mL of 50% methanol, and dried 100 °C/30 Torr/1 h to give 70.5 g of crude brown pellets, which were recrystallized from 500 mL of acetonitrile at 0 °C overnite to give huge yellow spars, mp 175–177.5 °C pc, 183–184 °C, 49.5 g (64%). Tlc on Whatman MK6F Silica Gel, ethyl acetate, UV, gave a single spot, R_f 0.72, **11**.

The product of an earlier run was recrystallized from 20 mL/g of 1:1 methanol:dibutyl ether. Anal. Calcd for $C_{30}H_{20}N_2O_3$: C, 71.43; H, 5.95; N, 8.33. Found by Micro-Analysis: C, 70.41; H, 5.70; N, 8.24. ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.22 (6H, t, $J = 7.0$), 3.45 (4H, q, 7.0), 5.06 (2H, s), 6.66 (2H, AA′XX′, $J = 9.5$), 7.91 (2H, AA′XX″, 9.5).

Synthesis of 4′-(Diethylamino)phenacylammonium Bromide Hydrobromide Hemihydrate (13). The phthalimide (**11**, 16.0 g, 0.476 mol) and potassium hydroxide (3.3 g of 85%, 2.80 g, 0.501 mol) in 135 mL of water and 30 mL of 1-propanol were boiled under reflux for 19 h, cooled in a water bath to 20 °C, and made up to pH 4.6 with 6 M hydrochloric acid. The liquid was decanted and the residual gum was crystallized from 75 mL of 95% ethanol, diluting with 75 mL of water, and keeping at 0 °C to give crystals, after drying them at 100 °C/20 Torr/1 h, of **N-[4′-(diethylamino)phenacyl]phthalamic acid (12)**, 11.75 g (73%), mp 144–145 °C dec (loss of water).

This and 158 mL of 40% hydrobromic acid were boiled under reflux overnight. The temperature was 120 °C at reflux to start and 118 °C at the end. The mixture was cooled in ice to 10 °C, the phthalic acid filtered off, and the filtrate evaporated at 5 Torr and 80 °C bath temp. To the solid residue was added 90 mL of abs ethanol with evaporation at 20 Torr, then 50 mL of toluene was added with evaporation at 20 Torr, then the mush was taken up in 60 mL of 2-propanol and diluted with 100 mL of ether. The product was collected and dried at 60 °C/20 Torr/18 h to get a crispy tan solid (**13**), mp 168–182 °C dec.

The product of an earlier run, purified by washing with 2-propanol, mp 177–180 °C dec, was assayed. Anal. Calcd for $C_{12}H_{20}N_2O\cdot\frac{1}{2}H_2O$: C, 38.22; H, 5.61; N, 7.43. Found: C, 37.99; H, 5.30; N, 7.60.

Synthesis of 5-(4-Diethylaminophenyl)-2-(4-cyanophenyl)oxazole (14). A mixture of 4′-(diethylamino)phenacylammonium bromide hydrobromide hemihydrate (**13**, 0.94 g, 0.0025 mol), 4-cyanobenzoic acid (0.37 g, 0.0025 mol), and 10 mL of phosphorus oxychloride was boiled under reflux for 16 h, allowed to cool to 60 °C, then quenched in 100 g of ice. Then sodium carbonate monohydrate were added to obtain pH 6.2, and the lot was filtered; the solid was washed with water, 50% methanol, then a little methanol, and air-dried overnight to give 0.60 g of crispy brown solid, which was then extracted from 5 cm of Merck Silica Gel 60 in a small Ace-Kau with a mixture of 30 mL of heptane and 10 mL of benzene; the extract was kept at −20 °C. The benzene froze, so after a slight warmup to melt it, the yellow solid was filtered as above, washed with heptane, and dried to give 0.185 g (25%), mp 148–150 °C. IR (CHCl$_3$, cm^{-1}) 2970 & 2930 & 2900 & 2867 (alCH), 2230 (cyano), 1603 (C=N, C=C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.23 (6H, t, $J = 7.0$), 3.43 (4H, q, $J = 7.0$), 6.73 (2H, d, $J = 8.7$), 7.29 (1H, s), 7.58 (2H, d, $J = 8.7$), 7.76 (2H, d, $J = 8.2$), 8.17 (2H, d, $J = 8.2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.2, 44.8, 111.7, 113.1, 114.7, 119.0, 121.1, 126.2, 131.9, 132.7, 148.6, 154.1, 158.1. Fl Em: $\lambda_{max} = 476$ nm, $\Phi_f = 0.69$.

Further extraction of the column gave 41 mg which was recrystallized from 1 mL of abs ethanol to give nice yellow blades, mp 150–151 °C. Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.68; H, 6.03; N, 13.24. Found: C, 74.85; H, 6.13; N, 13.01.

Synthesis of 4′-Bromophenacylammonium Bromide Dihydrate (16). Hexamethylene tetramine (49.2 g, 0.350 mol) was dissolved in 750 mL of chloroform, then 2,4′-dibromo-

acetophenone (97.4 g, 0.350 mol) was added all at once; the suspension was stirred overnight and the quaternary salt was collected, washed with 750 mL of chloroform, and dried at 60 °C/20 Torr/4 h. The product was treated with 900 mL of methanol and 120 mL of 48% hydrobromic acid at 20 °C for 2 days; solid was always present, so 600 mL of methanol was added, and the suspension was heated at 50 °C overnight and then at reflux for 1.5 h, cooled to 20 °C, and evaporated at a bath temperature of 50 °C to obtain a mushy solid, which was recrystallized from 700 mL of water to give **16**, 84.4 g (73%), mp 273−27 7C° dec (lit.[19] mp 260 °C dec).

Synthesis of 5-(4-Bromophenyl)-2-(4-cyanophenyl)oxazole (18). A mixture of 4′-bromophenacylammonium bromide dihydrate (**16**, 4.45 g, 0.0134 mol), 4-cyanobenzoyl chloride (2.27 g, 0.0134 mol), pyridine (1.2 mL, 1.2 g, 0.015 mol), and 50 mL of THF were stirred overnight and the solid amide **17** was collected, then slurried in 100 mL of water to which excess sodium bicarbonate was added, collected, and dried at 100 °C/20 Torr/1 h to give 3.03 g (66%) of amide **17**. This was boiled under reflux with 30 mL of phosphorus oxychloride for 2 h, allowed to cool to 20 °C, and quenched in 300 mL each of ice and water. After a few minutes, 50 mL of 50% w/w sodium acetate trihydrate was added. The organic solid was collected, washed with water, then methanol, and then was dried at 80 °C/20 Torr/1 h to give crude **18**, which was recrystallized from 30 mL of 2-methoxyethanol, again from 21 mL of xylenes, to give 1.91 g (44%) of small yellow needles, mp 210−212 °C. Anal. Calcd for $C_{16}H_9BrN_2O$: C, 59.10; H, 2.79; N, 8.62. Found: C, 58.82; H, 2.75; N, 8.54. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (1H, s), 7.62 (4H, s), 7.79 (2H, AA′XX′, J = 8.6), 8.21 (2H, AA′XX′, J = 8.6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.1, 118.7, 123.5, 124.9, 126.3, 126.7, 127.1, 131.3, 132.7, 1331, 151.9, 159.8.

Synthesis of Bis(4-methoxyphenyl)amine (19). In order of addition, *p*-anisidine (59.25 g, 0.481 mol), 4-bromoanisole (62.2 mL, 92.9 g, 0.497 mol), 1200 mL of toluene, tris-(dibenzylideneacetone)dipalladium(0) (3.18 g, 0.00347 mol), 1,1′-bis(diphenylphosphino)ferrocene (2.57 g, 0.00414 mol, Norquay Technologies, Inc.), and sodium *tert*-butoxide (60.9 g, 0.634 mol) were stirred and heated rapidly to 70 °C, then slowly to reflux (110−106 °C) for 24 h, and then cooled in a water bath to 20 °C, when 250 mL more toluene was added. The solids were filtered off and washed with 250 mL of toluene. The filtrates were evaporated, and the residue recrystallized from 750 mL of heptane to give 93 g (85% crude), which was extracted from 7.5 cm of Merck 10181 Silica Gel in a large Ace-kau with 1200 mL of cyclohexane. The extract was kept at 20 °C for 3 days to give white plates, which were collected, washed with 500 mL of hexane, and air-dried to yield 71.1 g (64%), mp 103−104 °C (lit.[20] mp 105 °C).

Synthesis of 2-(4-Cyanophenyl)-5-{4-[bis(4-methoxyphenyl)amino]phenyl} oxazole (20). A mixture of 5-(4-bromophenyl)-2-(4-cyanophenyl)oxazole (**18**, 6.50 g, 0.0200 mol), bis(4-methoxyphenyl)amine (**19**, 4.82 g, 0.0210 mol), 200 mL of toluene, tris(dibenzylideneacetone)dipalladium(0) (0.23 g, 0.00025 mol), 1,1′-bis(diphenylphosphino)ferrocene (0.19 g, 0.00034 mol), and sodium *tert*-butoxide (2.50 g, 0.026 mol) was treated as for **19** above. The toluene filtrates were chromatographed on a 4 × 16 cm column of Merck 10181 Silica Gel, with rejection of the toluene eluates. Dichloromethane eluates were rejected, then THF eluted **20** as a dark yellow oil after evaporation. This was crystallized from 100 mL of 1-butanol, and recrystallized from 1-propanol to give 5.00 g (53%) of dark yellow prisms, mp 165−167.5 °C. Calcd for $C_{30}H_{23}N_3O_3$: C, 76.09; H, 4.90; N, 8.88. Found: C, 75.60; H, 4.89; N, 8.69. ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (6H, s), 6.88 (4H, AA′XX′, J = 9.0), 6.97 (2H, AA′XX′, J = 9.0), 7.12 (4H, AA′XX′, J = 8.9), 7.35 (1H, s), 7.52 (2H, AA′XX′, J = 8.9), 7.77 (2H, AA′XX′, J = 8.7), 8.17 (2H, AA′XX′, J = 8.7). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 113.4, 118.9, 119.1, 119.9, 122.7, 125.8, 126.7, 126.9, 127.5, 131.7, 133.0, 140.4, 149.9, 153.4, 156.9, 158.7. UV−vis:

λ_{max} 302 nm (ϵ = 27 900), 402 (ϵ = 29 100). Fl Em: λ_{max} = 505 nm, Φ_f = 0.63.

Synthesis of Tetraethyl (*E*)-2-Butene-1,4-diphosphonate (22). (*E*)-1,4-Dichloro-2-butene (25.0 g, 0.200 mol) and triethyl phosphite (79 mL, 76.31 g, 0.500 mol, Williams & Wilkins Co.) were heated under an air-condenser whose effluent led to an ice-cooled dewar condenser. Reaction began at 150 °C, then, after an hour, a sudden exotherm to 193 °C occurred, while about 20 mL of chloroethane collected in the condenser. The residue was distilled thru a spray-trap/air condenser to give, after discarding a fore-run, a colorless oil, bp mostly 187−189 °C/0.55 Torr, 58.7 g (97%), d = 1.1265 at 24 °C (lit. 65%, bp 226 °C/15 Torr;[32] 93.5%, bp 149−152 °C/0.1−0.15 Torr[33]). ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (12H, dt, J = 7.2, $^4J_{PH}$ = 1.8), 2.36 (4H, m), 3.87 (8H, m), 5.38 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6 ($^3J_{PC}$ = 5.8), 30.7 ($^1J_{PC}$ = 137.6), 62.1 ($^2J_{PC}$ = 6.5), 124.5 ($^2J_{PC}$ = 3.7).

Synthesis of Tetraethyl 1,4-Xylylenediphosphonate (30). Triethyl phosphite (722 mL, 700 g, 4.56 mol) and 1,4-xylylene dichloride (100 g, 0.572 mol) were heated under a plain column to allow byproduct chloroethane to distill, which began at 147 °C and was complete after a few hours at 159 °C, 69 mL being captured by an ice-cooled dewar condenser. Most of the excess triethyl phosphite was distilled up to 180 °C, and the residue, at 90 °C, was poured into 1400 mL of hexane with stirring. Crystallization was complete at −2 °C to give, after drying at 22 °C/0.5 Torr/18 h, 211 g (98%) of white odorless plates, mp 75−77 °C. Recrystallization of an earlier batch from 10 mL/g of hexane, after decantation from a lower layer of polar impurity and keeping at −2 °C, gave 87% rec. of mp 76−78.5 °C (best lit. 100%, mp 73−74 °C,[34] 73−74 °C;[35] ^1HMR 60 MHz[36,37]).

Synthesis of Diethyl 9,9-Dipropylfluorene-2,7-dicarboxylate (34). A mixture of 9,9-dipropylfluorene-2,7-dicarboxylic acid[18] (**33**, 38.5 g, 0.1138 mol), 1 L of ethanol, and 10 mL of methanesulfonic acid was boiled under reflux for 44 h, cooled to 20 °C, and diluted with 2 L of water. The resulting suspension was made to pH $\approx$9 by addition of sodium carbonate monohydrate. The collected product was air-dried for 2 weeks to give 41.3 g (92%), mp 148−152 °C. The analytical sample was recrystallized from 20 mL/g of 95% ethanol, mp 149−152 °C. Calcd for $C_{25}H_{30}O_4$: C, 76.11; H, 7.67. Found: C, 76.38; H, 7.71. IR ($CHCl_3$, cm^{-1}) 3013 (ArCH), 2980 & 2960 & 2906 & 2870 & 2840 (alCH), 1700 (vs, C=O), 1606 (Ar C=C), 1283 & 1260 & 1237 & 1207 (vs, C−O).

Synthesis of 9,9-Dipropylfluorene-2,7-dimethanol (35). The Grignard reagent of 2,7-dibromo-9,9-dipropylfluorene[18] (**36**, 40.8 g, 0.100 mol) with magnesium (4.864 g, 0.200 mol, Reade RMC-3, 99.98%) was prepared in 400 mL of THF, then cooled in an ice bath. To the thick suspension was added DMF (15.5 mL, 14.62 g, 0.200 mol), and this was held at 40 °C for 1 h, by which time all lumps had broken up. At 36 °C 200 mL of 3 M hydrochloric acid was added with ice-cooling. The upper organic layer was dried over calcium chloride, then further with sodium sulfate, then evaporated to give 30.6 g (100% crude) of orange oily **9,9-Dipropylfluorene-2,7-dicarboxaldehyde (37)**. (A sample from an earlier run was chromatographed on Silica Gel, eluting with toluene, and the residue on evaporation crystallized from ethanol−water to give white solid, mp 111−112 °C.) With mechanical stirring, the 0.100 mol of crude **36** in 100 mL of toluene was treated with 65% sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 34 mL, 0.120 mol) in 200 mL of toluene, which caused

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an exotherm to 53 °C. An hour of stirring was followed by addition of a mixture of 100 mL of water, 100 mL of ice, and 85 mL of 12 M hydrochloric acid, slowly at first. At 50 °C the upper organic layer was separated and washed with 200 mL of warm water, then kept at −2 °C to obtain 16.6 g of **35**, mp 128−137 °C; this was recrystallized from 95 mL of toluene at 25 °C to obain, in two crops, 16.6 g (53%) of product, mp 135−137 °C. Calcd for $C_{21}H_{26}O_2 \cdot 0.1H_2O$: C, 81.25; H, 8.44. Found: C, 80.88; H, 8.46. IR ($CHCl_3$, cm^{-1}) 3600 (OH), 2935 (br, inter-bonded OH), 3005 (ArCH), 2960 & 2930 & 2906 & 2875 & 2840 (alCH), 1202 & 1003 (C−O str).

Synthesis of 2,7-Bis(chloromethyl)-9,9-Dipropylfluorene (38). A three-phase mixture of 250 mL of 12 M hydrochloric acid, 140 mL of toluene, and 9,9-dipropylfluorene-2,7-dimethanol (**35**, 14.1 g, 0.0454 mol) was stirred rapidly at 23 °C for 19 h. The lower acid layer was sucked out and replaced with 250 mL of acid. Two more hours of stirring seemed to indicate completion of the reaction by TLC on Whatman MK6F Silica Gel, CHCl₃, UV: no mono-Cl at R_f 0.14, di-Cl R_f 0.79. So 100 mL each of toluene and heptane were added, and the upper layer was washed with 250 mL of water and dried briefly with calcium chloride and evaporated to give a nice tan solid, which was recyrstallized from a minimum of 2-propanol to give white blades, mp 116−119.5 °C, 9.70 g (61%) (lit.[18] 64%, mp 115−117 °C).

Synthesis of 2,7-Bis(diethylphosphono)-9,9-dipropylfluorene (39). Triethyl phosphite (16 mL, 0.112 mol) was heated with 2,7-bis(chloromethyl)-9,9-dipropylfluorene (**37**, 9.70 g, 0.0279 mol) beyond a violent exotherm at 120 °C to reflux, which was maintained for 1 h, during which time the pot temperature went from 163 °C to 170 °C. This was allowed to cool below 100 °C and 80 mL of 2,2,4-trimethylpentane was added, while maintaining stirring, followed by an overnight sit at 20 °C. The product was collected, washed with 75 mL of 2,2,4-trimethylpentane, and dried to give gleaming white prisms, mp 125−127.5 °C, 13.59 g (88%) (lit. from di-Cl 90%, mp 126−128 °C, from di-Br 43%, mp 126−128 °C[18]).

Synthesis of 4-(Diphenylamino)benzaldehyde (23d). With use of a motor-driven Teflon paddle stirrer, 1.00 L of dry DMF in a water bath was treated below 15 °C with phosphorus oxychloride (75 mL, 122.6 g, 0.800 mol) in 1/5 portions, each in a thin stream. Warm water was then added to the bath to attain 30 °C in the flask, then triphenylamine was added rapidly (98.13 g, 0.400 mol) and the bath was heated to maintain 85−88 °C for a total of 3 h. The dark mixture was cooled in ice to 40 °C and quenched in 800 g each ice and water with propeller stirring, to which was then added 800 mL of 50% sodium acetate trihydrate w/w, followed by a few minutes of stirring and an overnight sit. The crude product was collected and slurried with a propeller in 1600 mL of 47.5% ethanol v/v for 15 min and re-filtered, and the damp solid was recrystallized from 1800 mL of 95% ethanol, decanted hot, and kept at 20 °C for 5 days, followed by 4 h at −2 °C. The brown needles were collected, washed with 250 mL of cold 95% ethanol, and dried 60 °C/20 Torr/20 h to give 92.8 g (85%) of brown needles, mp 132−134 °C (lit. no yield, mp[22] 132−133.5 °C).

Synthesis of Bis(4-methoxyphenyl)aminobenzonitrile (27). Added in the order given, bis(4-methoxyphenyl)amine (**19**, 21.4 g, 0.0933 mol), 4-bromoacetonitrile (6.1 g, 0.0887 mol), tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃, 1.02 g, 0.00112 mol], 1,1′-bis(diphenylphosphino)ferrocene (dppf, 0.83 g, 0.00149 mol, Norquay Technology), and sodium *tert*-butoxide (11.1 g, 0.116 mol) were heated to gentle reflux for 44 h at 111 °C. (Tlc on Whatman MK6F Silica Gel, ethyl acetate, UV, showed **19** at R_f 0.44 and **27** at R_f =0.80; no change between 21 and 44 h.) The solids were filtered off and washed with 2 × 50 mL of toluene. The filtrates were evaporated to 33.5 g of black oil which crystallized from 260 mL of 95% ethanol at −20 °C ovenite. This was diluted with 260 mL of methanol and the solid collected (24 g when air-dried) and a second crop

was obtained by further dilution with 800 mL of water and cooling at −20 °C to give 2 g. Combined, this was passed thru a 4 × 15 cm column of Merck 10181 Silica Gel in dichloromethane, followed by 1.5 L of this solvent. The eluate was evaporated to give 28 g of crystals, which were recrystallized from a mixture of 150 mL each of abs ethanol and methanol at −2 °C for 2 days to give tan prisms, mp 128−130 °C, 20.1 g (69%). Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.46; H, 5.35; N, 8.32. ¹H NMR (400 MHz, CDCl₃) δ 3.83 (6H, s), 6.81 (2H, AA′XX′, $J = 8.9$), 6.90 (4H, AA′XX′, $J = 9.1$), 7.12 (4H, AA′XX′, $J = 9.1$), 7.37 (2H, AA′XX′, $J = 8.9$). IR (CHCl₃, cm^{-1}) 3020 & 3000 (w, ArCH), 2980 & 2920 & 2870 & 2850 (alCH), 2218 (s, cyano), 1596 (s, C−N & C=C), 1235 & 1205 (vs, Ar−O & al-O), 1162, 1111, 1040 (s, C−O−C).

Synthesis of Crude 4-[Bis(4-methoxyphenyl)amino]-benzaldehyde (23e). With cannulae and septa, diisobutyla-luminum hydride (DIBALH, 20% w/w in toluene, 41 mL, 0.050 mol) was pushed into a pressure-equalized addition funnel. Then 4-[bis(4-methoxyphenyl)amino]benzonitrile (**27**, 11.0 g, 0.0333 mol) was added to a flask in a bath below the funnel, followed by 330 mL of ether, in which the nitrile was only partially soluble. Dry ice and 1-propanol were placed in the bath (temperature −56 °C), then the DIBALH was added dropwise below −50 °C. The mixture was allowed to warm to −30 °C during which time most solid dissolved. Protected by Drierite tubes, the reaction flask was placed in a −20 °C freezer overnite. In a 1-L flask a quench mixure of 125 mL each of ice and water along with 25 mL of acetic acid was purged with argon and the liquid portion of the reaction mixture was pumped in using cannulae and septa. The quenchate was stirred an hour and the organic layer was evaporated to an oil, treated with 100 mL benzene, and evaporated again to yield 10.6 g (96% crude) of yellow oil, which would not crystallize, so it was made up to 50 mL with dry DMF for use in Wadsworth−Emmons reactions below. IR (CHCl₃, cm^{-1}) 3030 & 3010 (ArCH), 298 & 2960 & 2910 & 2840 (w, alCH), 2840 (w, ald. C−H), 1677 (s, br, C=O), 1590 (vs, C−N & C=C), 1238 & 1212 (vs, Ar−O & al-O), 1159 vs & 1104 & 1031 (C−O−C).

General Procedure for Wadsworth−Emmons Reactions To Form Hexatrienes 24a−d, 26a−c; Distyrylbenzenes 31d−g, 32a−e; and Distyrylfluorenes 40a,d,e, All (E). The aldehyde (0.0933 mol) and the diphosphonate (0.0444 mol) in 300 mL of DMF were treated with a solution of potassium *tert*-butoxide (0.175 mol) in 100 mL of DMF at 20−50 °C with cooling, if necessary. The yellow products usually separated. After the reaction was kept at 20 °C overnight, it was poured into 1 L of methanol and stirred 30 min, and the product was collected, washed with methanol, and air-dried to give 70−100% yields (except **32a**) of crude alkene, which was extracted from adsorbent in a large Ace-Kau, and the extract was cooled to give pure product, typically in 76−90% yield. The adsorbent, solvent, yield when this exact method was used, assays, and NMR spectra are given below. The absorption and fluorescence data, as well as that of related fluors, are given in Table 1 for the hexatrienes, Table 2 for the distyrylbenzenes, and Table 3 for the distyrylfluorenes, all in toluene unless otherwise indicated.

1,6-Di-4-biphenylyl-1,3,5-hexatriene (24b). From **23b** and **24**. Acidic alumina, toluene, mp 303−308 °C. Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 94.09; H, 6.04. Too insoluble for NMR.

1,6-Bis[7-(4-*tert*-butylphenyl)-9,9-dipropyl-2-fluorenyl]-1,3,5-hexatriene (24c). From **23c** and **24**. Neutral alumina, heptane, recryst. 2-butoxyethanol/2-propanol, mp 278−282 °C. Anal. Calcd for $C_{64}H_{72}$: C, 91.37; H, 8.63. Found: C, 91.73; H, 8.40. ¹H NMR (400 MHz, CDCl₃) δ 0.73 (20H, m), 1.41 (18H, s), 2.03 (8H, m), 6.64 (2H, dd, $J = 7.0$, $J = 3.1$), 6.73 (2H, d, $J = 15.4$), 7.02 (2H, ddd, $J = 15.4$, $J = 7.0$, $J = 3.1$), 7.60 (20H, m). ¹³C NMR (100 MHz, CDCl₃) δ 14.9, 17.6, 31.8, 35.0, 43.3, 55.7, 120.3, 120.9, 121.8, 126.1, 126.2, 129.1, 129.2, 133.6, 133.9, 136.8, 139.1, 140.2, 140.3, 141.0, 150.6, 151.9, 152.0.

1,6-Bis[4-(diphenylamino)phenyl]-1,3,5-hexatriene (24d). From **23d** and **24**. Silica Gel, toluene; evaporated, recrystallized from 1-butanol/xylenes, mp 235−238 °C (lit.[38]). Anal. Calcd for $C_{42}H_{34}N_2$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.35; H, 6.02; N, 5.32. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.50 (2H, dd, J = 7.1, J = 3.1), 6.54 (2H, d, J = 15.4), 6.81 (2H, ddd, J = 15.4, J = 7.1, J = 3.1), 7.04 (8H, m), 7.13 (8H, m), 7.29 (12H, m). ^{13}C NMR (100 MHz, CDCl$_3$) δ 123.4, 123.9, 124.9, 127.6, 128.2, 129.7, 132.1, 132.2, 133.5, 147.5, 147.9.

1,1,6,6-Tetraphenyl-1,3,5-hexatriene (26a). From **25a** and **26**. Acidic alumina, heptane, mp 194−195 °C pc, 200−207 °C; best 206−207 °C (lit. 185 °C,[39] 208 °C,[40] 192−196 °C,[41] 202−203 °C,[42] ^{1}H NMR 90 MHz[43]).

1,1,6,6-Tetra-4-Biphenylyl-1,3,5-hexatriene (26b). From **25b** and **26**. Neutral alumina, toluene, mp s. 317 °C, 324−330 °C pc, 334−337 °C dec. Anal. Calcd for $C_{30}H_{24}$: C, 94.15; H, 5.85. Found: C, 94.03; H, 5.58. ^{1}H NMR (400 MHz, pyridine-d_5) δ 5.70 (4H, s), 7.45 (4H, t, J = 8.1), 7.53 (8H, t, J = 8.1), 7.79 (8H, d, J = 8.1), 7.85 (8H, d, J = 8.1), 8.07 (8H, d, J = 8.1). Too insoluble for ^{13}C.

1,4-Bis[9-fluorenylidene]-2-butene (26c). From fluorenone and **26**. Mp 333−337 °C dec (lit. mp 331.5−333 °C,[25] 340 °C[44]). Too insoluble for NMR.

1,4-Bis[4′-(diphenylamino)styryl]benzene (31d). From **30** and **23d**. Florisil, 1-chlorobutane, recrystallized from 1-butanol, 87%, mp 198−199 °C pc, 203−205 °C. The product of an earlier run was recrystalllized from 1-pentanol, Anal. Calcd for $C_{46}H_{36}N_2$·$0.25C_5H_{12}O$: C, 88.83; H, 6.15; N, 4.39. Found: C, 88.71; H, 6.36; N, 4.21. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (20H, m), 7.28 (4H, AA′XX′, J = 8.6), 7.30 (4H, AA′XX′, J = 8.5), 7.41 (4H, AA′XX′, J = 8.6), 7.50 (4H, s). ^{13}C NMR (100 MHz, CDCl$_3$) δ 123.5, 124.0, 124.9, 127.0, 127.1, 127.8, 128.3, 129.7, 132.0, 137.1, 147.8, 148.0. τ_f = 1.86 ns.

1,4-Bis[4′-bis(4-methoxyphenyl)aminostyryl]benzene (31e). From **30** and **23e**. Extracted from Soxhlet with hexanes, recrystallized from dibutyl ether, then 1-pentanol, mp 175 °C pc, 178−181 °C. Anal. Calcd for $C_{50}H_{44}N_2O_4$·$0.25C_5H_{12}O$: C, 81.49; H, 6.02; N, 3.80. Found: C, 81.18; H, 6.20; N, 3.71. UV−vis and Fl em, see Figure 4. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.82 (12H, s), 6.86 (8H, AA′XX′, J = 9.0), 6.93 (4H, AA′XX′, J = 8.7), 6.95 (2H, d, J = 16.0), 7.06 (2H, d, J = 16.0), 7.09 (8H, AA′XX′, J = 9.0), 7.34 (4H, AA′XX′, J = 8.7), 7.47 (4H, s). Too insoluble for ^{13}C. τ_f = 2.25 ns.

1,4-Bis[4′-(dimethylamino)styryl]benzene (31f). From **30** and **23f**. Recrystallized from diethylene glycol/diphenylmethane, 86%, mp 325−332 °C dec (lit.[17,45]). Anal. Calcd for $C_{26}H_{28}N_2$: C, 84.74; H, 7.66; N, 7.60. Found: C, 84.47; H, 7.38; N, 7.50. ^{1}HMR (400 MHz, CDCl$_3$) δ 3.01 (12H, s), 6.75 (4H, bd, J = 8.3), 6.93 (2H, d, J = 16.3), 7.07 (2H, d, J = 16.3), 7.44 (4H, d, J = 8.3), 7.46 (4H, s). Too insoluble for ^{13}C.

1,4-Bis[2-(9-julolidinyl)ethenyl]benzene (31g). From **30** and **23g**,[9] recrystallized from DMA, mesitylene, chromatographed on Silica Gel with dichloromethane in dim light, evaporated, mp 240−248 °C dec Anal. Calcd for $C_{34}H_{36}N_2$·0.25-CH_2Cl_2: C, 81.55; H, 7.32; N, 5.53. Found: C, 81.88; H, 6.81; N, 5.26. ^{1}H NMR (400 MHz, CDCl$_3$):δ 2.01 (8H, q, J = 6.1), 2.80 (8H, t, J = 6.1), 3.19 (8H, t, J = 6.1), 6.86 (2H, d, J = 16.4), 6.97 (2H, d, J = 16.4), 7.00 (4H, s), 7.42 (4H, s). ^{13}C NMR (100 MHz, CDCl$_3$) δ 22.5, 28.1, 50.4, 121.8, 123.8, 125.5, 125.7, 126.5, 128.7, 137.1, 138.1, 143.1.

1,4-Bis(2-phenylstyryl)benzene (32a). From **30** and **25a**. Neutral alumina, heptane:toluene 10:1 (27%, 0% by normal method), mp 192−194 °C (lit. mp 193−194 °C,[41] 188−189 °C[46]). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.82 (4H, s), 6.90 (2H, s), 7.21 (4H, m), 7.32 (16H, m). ^{13}C NMR (400 MHz, CDCl$_3$) δ 127.8, 127.9, 128.0, 128.3, 128.6, 129.0, 129.6, 130.8, 136.3, 140.8, 142.9, 143.9.

1,4-Bis[4′-(dimethylamino)-2-phenylstyryl]benzene (32b). From **30** and **25b**. Recrystallized from 2-ethoxyethanol, mesitylene twice, then DMA to obtain mp 247−248 °C pc, 249−252°. Anal. Calcd for $C_{38}H_{36}N_2$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.64; H, 6.94; N, 5.53. ^{1}H NMR (400 MHz, CDCl$_3$; mixture of E and Z isomers in 3:1 ratio determined by integration of methyl peaks; when signals for the same proton in both isomers were resolved, both are listed with the major component appearing first) δ 2.98 & 3.00 (12H, s), 6.67 (4H, m), 6.74 & 6.95 (4H, s), 6.78 & 6.76 (2H, s), 7.19 & 7.07 (4H, AA′XX′, J = 9.2), 7.32 & 7.21 (10H, m).

1,4-Bis{2,2-[bis(4-dimethylamino)phenyl]ethenyl}-benzene (32c). From **30** and **25c**. Recrystallized from 2-ethoxyethanol, 2-butoxyethanol, then mesitylene to obtain mp 244−247 °C pc, 249−253 °C. Anal. Calcd for $C_{42}H_{46}N_4$: C, 83.26; H, 7.49; N, 9.25. Found: C, 83.17; H, 7.66; N, 8.97. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.98 (6H, s), 3.00 (6H, s), 6.67 (2H, s), 6.68 (8H, AA′XX′, J = 8.8), 6.89 (4H, s), 7.10 (4H, AA′XX′, J = 8.8), 7.23 (4H, AA′XX′, J = 8.8). ^{13}C NMR (100 MHz, CDCl$_3$) δ 40.9, 41.0, 112.3, 112.6, 124.4, 129.1, 129.2, 131.8, 133.2, 136.6, 142.5, 150.0, 150.3.

1,4-Bis{2,2-[bis(4-methoxyphenyl)ethenyl]}benzene (32d). From **30** and **25d**. Recrystallized from dibutyl ether, mp 166.5−169.5 °C (90%). Anal. Calcd for $C_{38}H_{34}O_4$: C, 82.28; H, 6.18. Found: C, 82.39; H, 6.14. ^{1}HMR (400 MHz, CDCl$_3$) δ 3.84 (6H, s), 3.86 (6H, s), 6.76 (2H, s), 6.84 (4H, s), 6.85 (4H, AA′XX′, J = 8.8), 6.87 (4H, AA′XX′, J = 8.8), 7.12 (4H, AA′XX′, J = 8.8), 7.25 (4H, AA′XX′, J = 8.8). ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 55.7, 113.9, 114.3, 126.4, 129.3, 129.4, 133.2, 136.4, 137.0, 141.9, 159.3, 159.6.

1,4-Bis(fluorenylidenemethyl)benzene (32e). From **30** and fluorenone. Recrystallized from DMF, mp 215−217.5 °C (lit. mp 205−206 °C,[47] 212−214 °C[48]). Mass spectrum.[49] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (2H, dt, J = 1.3, J = 7.3), 7.37 (2H, dt, J = 7.6, J = 1.0), 7.38 (2H, dt, J = 7.3, J = 1.3), 7.43 (2H, dt, J = 7.3, J = 1.0), 7.43 (4H, s), 7.76 (6H, m), 7.78 (2H, s), 7.85 (2H, td, J = 7.3, J = 1.0). ^{13}C NMR (100 MHz, CDCl$_3$) δ 120.1, 120.3, 120.7, 124.8, 127.1, 127.2, 127.5, 128.7, 129.1, 130.0, 136.9, 137.1, 137.3, 139.6, 139.9, 141.8.

9,9-Dipropyl-2,7-distyrylfluorene (40a).[18] ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.74 (10H, m), 2.04 (4H, m), 7.22 (4H, AB, J = 16.4), 7.30 (2H, tt, J = 1.1, J = 7.4), 7.41 (4H, dd, J = 7.4, J = 7.8), 7.53 (4H, m), 7.58 (4H, dd, J = 1.1, J = 7.8), 7.69 (2H, dd, J = 1.5, J = 7.0). ^{13}C NMR (400 MHz, CDCl$_3$) δ 14.9, 17.6, 43.3, 55.6, 120.3, 121.1, 126.2, 126.9, 127.9, 128.4, 129.1, 129.7, 136.7, 137.4, 141.0, 152.0.

1,4-Bis[4′-bis(diphenylamino)styryl]-9,9-dipropylfluorene (40d). From **23d** and **39**. Neutral alumina, methylcyclohexane, lemon-yellow solid, mp 262 °C pc, 266−268 °C (83%). Anal. Calcd for $C_{59}H_{52}N_2$: C, 89.81; H, 6.64; N, 3.55. Found: C, 89.24, 89.26; H, 6.51, 6.55; N, 3.38, 3.35. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.73 (10H, m), 2.03 (4H, m), 7.07 (4H, tt, J = 7.3, J = 1.3), 7.10 (4H, AA′XX′, J = 8.5), 7.14 (4H, AB, J = 16.4), 7.15 (8H, dd, J = 1.3, J = 8.8), 7.30 (8H, dd, J = 7.3, J = 8.3), 7.45 (4H, AA′XX′, J = 8.5), 7.50 (4H, m), 7.67 (2H,

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dd, $J = 0.8$, $J = 7.6$). ^{13}C NMR (400 MHz, CDCl$_3$) δ 14.9, 17.6, 43.3, 55.6, 120.2, 120.9, 123.4, 124.0, 124.9, 125.9, 127.7, 127.9, 128.1, 129.7, 132.2, 136.9, 140.8, 147.6, 148.0, 151.9. $\tau_f = 1.73$ ns.

1,4-Bis[4′-bis(4-methoxyphenyl)aminostyryl]-9,9-dipropylfluorene (40e). From **23e** and **39**, mp 236−238 °C (100% crude). Extracted from a Soxhlet with 1-chlorobutane and kept 3 days at 20 °C, mp 225 °C pc, 239−240 °C (76%). Anal. Calcd for C$_{63}$H$_{60}$N$_2$O$_4$: C, 83.23; H, 6.65; N, 3.08. Found: C, 83.71; H, 6.43; N, 3.10. ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.71 (10H, m), 2.01 (4H, m), 3.83 (12H, s), 6.87 (8H, AA′XX′, $J = 9.1$), 6.94 (4H, AA′XX′, $J = 8.5$), 7.08 (4H, AB, $J = 16.8$), 7.10 (8H, AA′XX′, $J = 9.1$), 7.38 (4H, AA′XX′, $J = 8.5$), 7.47 (4H, m), 7.64 (2H, dd, $J = 1.0$, $J = 7.6$). $\tau_f = 2.05$ ns.

Supporting Information Available: ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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