

Electronic Absorption and Emission Spectral Data and Fluorescence Quantum Yields of Bridged *p*-Oligophenylenes, Bi- to Deciphenyls, and Related Furans and Carbazoles

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Absorption and fluorescence emission spectral data, as well as fluorescence quantum yields (Φ_f), were determined for 41 *p*-oligophenylene compounds containing 2–6, 8, and 10 benzene rings. Of 29 compounds containing carbon-bridged rings (fluorenes), 28 were dialkylated on each bridge for improved solubility and photostability. Absorption maxima for oligophenylenes were observed at wavelengths as long as 366 nm, emission maxima to 437 nm, and molar extinction coefficients (ϵ) as large as 153,000 L/mol-cm; all three exceeded predicted maximum values for the corresponding unbridged oligophenylenes. The substitution of furan for benzene or carbazole for a fluorene (two examples each) bathochromically shifted absorption and emission maxima. Dialkylated carbon bridges bathochromically shifted absorption and emission maxima, and lowered Φ_f in biphenyl and in one terphenyl analogue, but appeared to cause no diminution of Φ_f in higher oligophenylenes. Bis(2-methoxyethyl) substitution on the bridges, incorporated to provide solubility in polar solvents, lowered Φ_f in all examples. Tertiary alkyl substituents on terminal rings bathochromically shifted the absorption and emission maxima and generally increased Φ_f . The “loose bolt” effect, which lowers Φ_f in mononuclear substituted benzenes, may operate in 9,9-dialkylfluorenes, but not in 2,7-di-*t*-butylfluorene or in higher oligophenylenes. Cyclic ether and methoxy substituents as auxofluors on terminal rings generally bathochromically shifted absorption and emission maxima and increased ϵ and Φ_f . Cyano substituents bathochromically shifted absorption and emission maxima, and increased ϵ , but lowered Φ_f slightly.

KEY WORDS: *p*-Oligophenylenes; biphenyls; fluorenes; terphenyl; quaterphenyl; quinquiphenyl; sexipheynyl; octiphenyl; deciphenyls; furans; carbazoles; fluorescence; quantum yields; absorption; emission spectra; auxofluors.

INTRODUCTION

Oligophenylenes with high fluorescence quantum yields (Φ_f) continue to be of interest as laser dyes [1]

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and as scintillation fluors [2,3]. We and others have prepared a variety of terphenyls, quaterphenyls, and higher *p*-oligophenylenes [4–14]. To achieve the synthesis of soluble compounds with useful stability, we focused on molecules with *o,o'*-bridging between adjacent benzene rings (fluorenes) in which the bridging carbon always contained two alkyl substituents. Others concentrated on molecules with alkyl substitution on the rings but unsubstituted bridges.

As clearly pointed out [6], two obligatory properties of a good laser dye are large values of the molar extinction coefficient of absorption (ϵ) and Φ_f . In the design of new fluors, we sought as auxofluors those functional groups which would most enhance ϵ and Φ_f without compromising solubility or photochemical stability. Pavlopoulos and Hammond reported that amino groups on oligophenylenes caused instability [15]; therefore, we did not use them. We now report the absorption and emission data for a collection of 41 *p*-oligophenylenes containing 2–6, 8, and 10 benzene rings variously substituted with *t*-alkyl, alkoxy, and cyano groups. These include four heterocyclic analogues of oligophenylenes, two carbazoles, and two furans.

In his compendium of fluorescence data for aromatic compounds, Berلمان [4] chose to measure Φ_f values only in dilute cyclohexane solution. His reference compound, 9,10-diphenylanthracene (DPA), was assigned a Φ_f of 1.00 even though he acknowledged that there were some reasons to assign a lower value. Birks had compiled a mean value of 0.83 for the Φ_f of DPA in various solvents [16]. Morris *et al.* [17] subsequently determined that for DPA in nitrogen-saturated cyclohexane $\Phi_f = 0.86$. This value was within the experimental error of a recent determination by chemical actinometry of $\Phi_f = 0.90 \pm 0.004$ in deaerated cyclohexane [18]. Meech and Phillips give $\Phi_f = 0.93 \pm 0.03$ for DPA in four nonpolar solvents [19], apparently for freeze-pump-thaw degassed solutions. In this paper, we have chosen to use Morris' value of $\Phi_f = 0.86$ for DPA in nitrogen-bubbled solutions as the reference standard for the 41 compounds reported in Table I. To allow comparison with earlier work, we have included in Table II comparable data for five simple oligophenylenes with Φ_f values adjusted lower ($\times 0.86$) from the original [4]. Our earlier data, which were referenced to terphenyl [10–14], need adjusting higher ($\times 1.04$) to correspond to the value $\Phi_f = 0.80$ which appears for terphenyl in Table II.

The triplet absorption spectrum of fluor 32 has been reported [20].

EXPERIMENTAL

Materials. The syntheses of the fluors have been described in general terms [11]. Fluor 1 was purchased from Lancaster Synthesis, Ltd. The furan-containing fluors 34 and 35 were described in detail in a report [21] and the intermediate 2-(4-methoxyphenyl)furan for 35 has been reported [22]. As one key step in purification, all fluors were subjected to at least one chromatographic

extraction from alumina and/or Silica GelTM with a non-polar solvent (hexane, heptane, 1,1,2-trichlorotrifluoroethane, cyclohexane, pentenes) in an Ace-Kauffman Column [23] (Ace Glass Co., Vineland, NJ). Carbon and hydrogen assays were obtained and were in satisfactory agreement with calculations. Proton magnetic resonance spectra were measured for all of the fluors and were in excellent agreement with theory.

The cyclohexane used as the solvent for determination of spectra was "Distilled-In-Glass" grade from Burdick & Jackson.

The 9,10-diphenylanthracene was obtained from Polysciences, Inc., Warrington, PA. Other common vendors did not have pure material. The nitrogen used for purging the DPA solution was "Prepurified grade."

Methods. The absorption spectra, in air-saturated cyclohexane unless indicated otherwise, were determined on $\approx 10^{-5}$ M solutions in 1-cm path-length cells (far UV silica) using a Shimadzu UV265 spectrophotometer. This instrument was checked against a Cary 15 thought to be in good operating condition by observing the 206-nm band of Fluor 10 in both instruments; the wavelength agreed within 1 nm and the absorbance within 2%. The peak wavelengths listed in Table I were taken from these spectra.

For determination of Φ_f , the air-saturated solutions with which absorption peak wavelengths were determined were diluted to an absorbance of ≈ 0.1 to minimize self-absorption; thus no correction for self-absorption was used. More exact values of absorbance were found in silica cells of 10-cm path length and used for calculation of Φ_f . Beam divergence in the Shimadzu UV265 was checked by means of a reflective card and did not exceed the end window diameter of the 10-cm cells. The dilute solution method was used to determine Φ_f with a Farrand Spectrofluorometer Mk. I rebuilt to produce corrected spectra to 750 nm by Optical Technology Devices, Elmsford, NY. The reference standard was 9,10-diphenylanthracene (DPA) in nitrogen-saturated cyclohexane ($\Phi_{fstd} = 0.86$). The working equation was [24]

$$\Phi_{fSpl} = (\Phi_{fstd.}) (\text{Area}_{spl.}) (\text{Absorbance}_{std.}) / (\text{Area}_{std.}) (\text{Absorbance}_{spl.})$$

Areas of emission spectra were determined to $\pm 2\%$ with a planimeter (Los Angeles Scientific Instrument Co. Model L20M). The fluorescence emission peak wavelengths in Table I were taken from these same spectra. The absorption band used for excitation of each fluor is indicated in Table I, since certain fluors bearing rotatable auxochromic groups do exhibit emission band shifts at different excitation wavelengths [25].

Table I. Photophysical Properties of New Oligophenylene Fluors

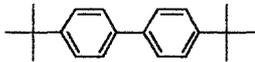
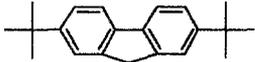
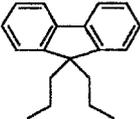
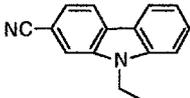
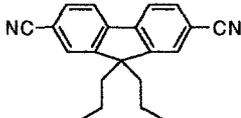
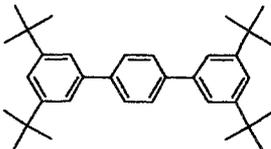
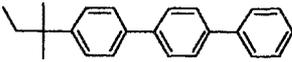
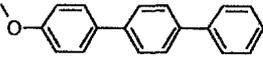
Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
1	4,4'-Di- <i>t</i> -butylbiphenyl 	212 (24,100) 256 ^f (24,700)	304 312m	0.26
2	2,7-Di- <i>t</i> -butylfluorene 	214 (27,800) 272 (29,200) 281 ^f 296 (10,200) 308 (13,100)	333 348m 364	0.70
3	9,9-Dipropylfluorene 	209 (48,900) 264 ^f (17,800) 292 (7,500) 304 (12,700)	309m 320sh	0.36 0.42 ^g
4	2-Cyano-9-ethylcarbazole 	223 (15,700) 245 (30,000) 250 (30,00) 260 (24,400) 294 (12,000) 300 (14,400) 306 ^f (24,400) 349 (3,200) 366 (4,200)	373m 392 415sh	0.12
5	2,7-Dicyano-9,9-dipropylfluorene 	210 (11,900) 222 (7,780) 231 (3,624) 239 (2,685) 281 (7,440) 292 ^f (9,710) 305 (7,020) 312 (6,260) 319 (12,100)	324m 339 355sh	0.32
6	3,5,3'',5''-Tetra- <i>t</i> -butyl- <i>p</i> -terphenyl 	217 (44,800) 277 ^f (33,600) 281 (29,000) ^b	336 349m 367sh	0.58
7	4- <i>t</i> -Amyl- <i>p</i> -terphenyl 	214 (34,500) 279 ^f (35,100) 287 (33,000) ^b	336 349m 365sh	0.65
8	4-Methoxyterphenyl 	286 ^f (39,000) ^c 291 (36,000,	338 353m 373sh	0.70

Table I. Continued

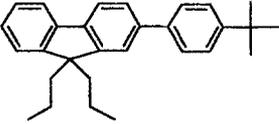
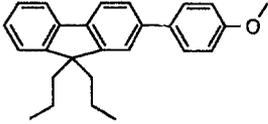
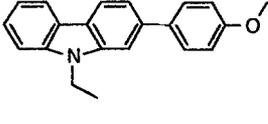
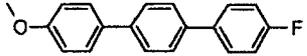
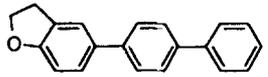
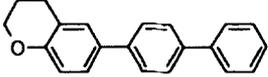
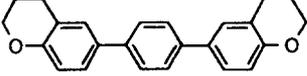
Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
9	2-(4- <i>t</i> -Butylphenyl)-9,9-dipropylfluorene 	218 (40,400) 293 ⁱ (34,600) 314 (33,100)	314m 357 374sh	0.65
10	2-(4-Methoxyphenyl)-9,9-dipropylfluorene 	216 (47,400) 293 (40,100) 304 ⁱ 315 (40,200)	345m 361 381sh	0.41
11	9-Ethyl-2-(4-methoxyphenyl)carbazole 	212 (25,000) 228 (26,000) 263 (50,000) 304 ⁱ 310 (30,700)	366 383m 405sh	0.22
12	4,4''-Dimethoxyterphenyl 	293 ⁱ (44,000) ^c	345 360m 376sh	0.64 0.68 ^b
13	4-Fluoro-4''-methoxyterphenyl 	215 (31,500) 281 ⁱ (32,500) 291 (35,000) ^b	338 352m 376sh	0.57
14	4-Cyano-4''-methoxyterphenyl 	305 ⁱ (34,000)	359 377m 398sh	0.48
15	5-(4-Biphenyl)-2,3-dihydrobenzofuran 	289 ⁱ (32,000) ^c	377 ^c	0.66
16	6-(4-Biphenyl)-2,3-dihydro-4H-benzopyran 	214 (30,300) 289 ⁱ (30,900)	344 359m 379sh	0.62
17	6,6'-(1,4-Phenylene)bis (2,3-dihydro-4H-benzopyran) 	211 (41,300) 295 ⁱ (33,900)	332s 351m 366 385sh	0.60 0.72 ^a
18	4,4''-Di- <i>t</i> -amyl- <i>p</i> -terphenyl 	208 (54,000) 285 ⁱ (38,000) 289 (43,000) ^b	338 354m 370sh	0.85

Table I. Continued

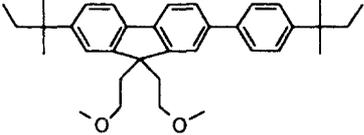
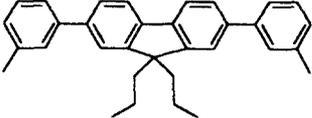
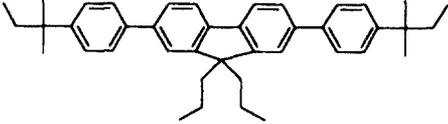
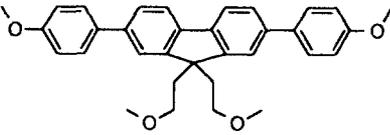
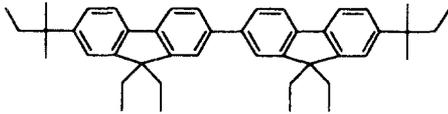
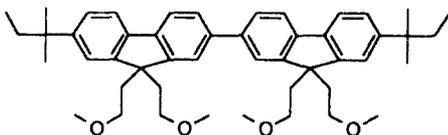
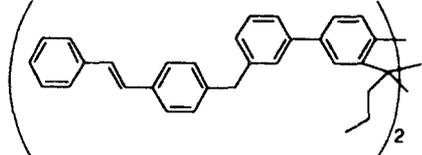
Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
19	2- <i>t</i> -Amyl-7-(4- <i>t</i> -amylphenyl)-9,9-bis(2-methoxyethyl)fluorene 	213 (54,200) 297 (36,990) 318 ⁱ (36,800) 299 (35,000) ^b 318 (35,000) ^b	345 360m 377sh	0.71
20	2,7-Bis(3-methylphenyl)-9,9-dipropylfluorene 	215 (45,400) 306 (29,700) 327 ⁱ (38,200)	363m 380 400sh	0.75
21	2,7-Bis(4- <i>t</i> -amylphenyl)-9,9-dipropylfluorene 	212 (61,000) 328 ⁱ (52,000)	368m 386 407sh	0.92
22	9,9-Bis(2-methoxyethyl)-2,7-bis(4-methoxyphenyl)fluorene 	214 (53,800) 321 ⁱ (58,000) 332 (49,300)sh	371m 389 412sh 440sh	0.61
23	7,7'-Di- <i>t</i> -amyl-9,9,9',9'-tetraethyl-2,2'-bifluorene 	214 (65,000) 302 (39,700) 331 ⁱ (62,000)	371m 390 409 434sh	0.85
24	7,7'-Di- <i>t</i> -amyl-9,9,9',9'-tetrakis(2-methoxyethyl)-2,2'-bifluorene 	214 ^d 331 ⁱ	371m 390 409 437sh	0.61
25	2,7-Bis[3-(4- <i>trans</i> -stilbenylmethyl)phenyl]-9,9-dipropylfluorene 	215 (103,000) 300 ⁱ 306 (66,000)sh 327 (80,000)	339 359m 380	0.08

Table I. Continued

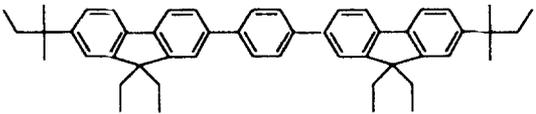
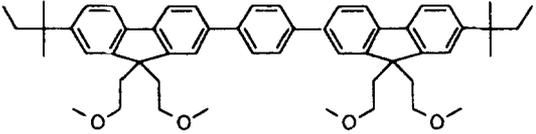
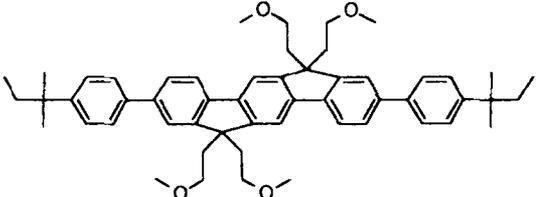
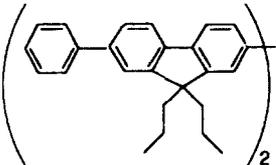
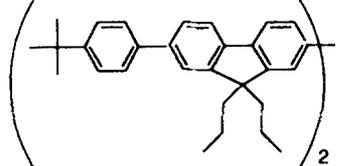
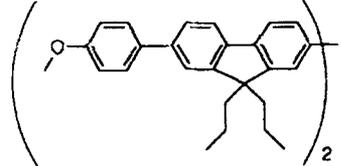
Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
26	1,4-Bis(7- <i>t</i> -amyl-9,9-diethyl-2-fluorenyl)benzene 	226 (46,000) 252 (11,000) 332' (76,000)	381m 400 422 450s	1.00
27	1,4-Bis[7- <i>t</i> -amyl-9,9-bis(2-methoxyethyl)2-fluorenyl]benzene 	214 (78,000) 332' (76,000)	380m 399 421 452s	0.90 0.86
28	2,8-Bis(4- <i>t</i> -amylphenyl)-6,6,12,12-tetrakis((2-methoxyethyl)indeno[1,2- <i>b</i>]fluorene) 	206 (61,000) 214 (66,700) 247 (23,900) 322 (34,500) 353' (75,600) 366 (71,700)	390m 409 433s	0.86
29	7,7'-Diphenyl-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	214 (67,200) 256 (16,400) 346' (74,500)	387m 408 430sh	1.02
30	7,7'-Bis(4- <i>t</i> -butylphenyl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	216 (200,000) 269 (115,000) 293 (76,000) 305 (88,000) 312 (70,000) 346' (77,000)	395m 417 441sh	0.92
31	7,7'Bis(4-methoxyphenyl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	214 (67,700) 262 (14,600) 350' (73,900)	395m 415 441sh	1.02

Table I. Continued

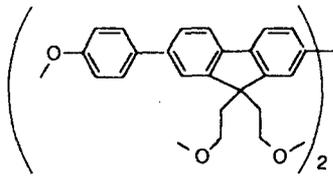
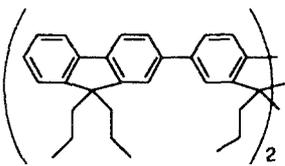
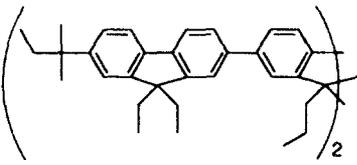
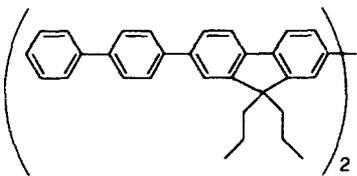
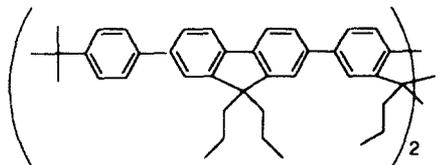
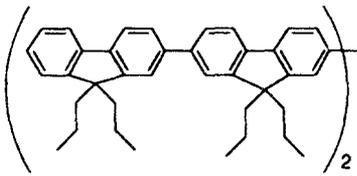
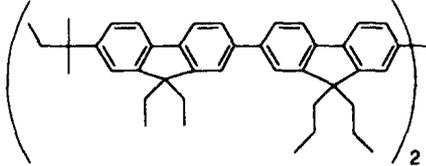
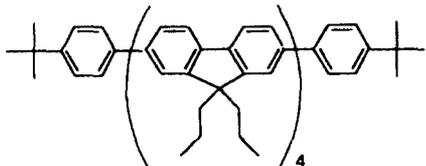
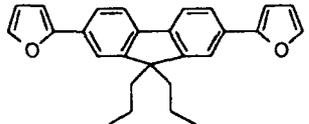
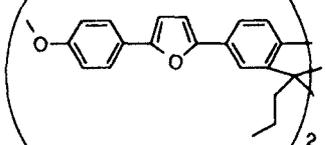
Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
32	7,7'-Bis(4-methoxyphenyl)-9,9,9',9'-tetrakis(2-ethoxyethyl)-2,2'-bifluorene 	349 ⁱ 360 (90,000) ^e	395m 416 441sh	0.95
33	9,9-Dipropyl-2,7-bis(9,9-dipropyl-2-fluorenyl)fluorene 	214 (90,900) 265 (25,800) 350 ⁱ (90,800)	396m 417 443sh	0.91
34	9,9-Dipropyl-2,7-bis(7- <i>t</i> -amyl-9,9-diethyl-2-fluorenyl)fluorene 	216 (84,000) 259 (12,000) 268 (19,000) 351 ⁱ (93,000)	400m 420 445sh	0.93
35	7,7'-Bis(4-biphenyl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	357 ⁱ (98,000) ^f	402m 423 449sh	0.92
36	7,7''-Bis(4- <i>t</i> -amylphenyl)-9,9,9',9'',9''-hexapropyl-2,2':7'2''-terfluorene 	215 (109,000) 285 (25,000) 362 ⁱ (122,000)	408m 430 456sh	0.90
37	7,7'-Bis(9,9-dipropyl-2-fluorenyl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	214 (94,400) 286 (16,400) 360 ⁱ (107,500)	407m 430 460sh 493sh	0.89

Table I. Continued

Fluor No.	Name and Structure	Abs. λ max, nm (ϵ)	Fluor em. λ , nm ^a	Φ_f
38	7,7'-Bis(7- <i>t</i> -amyl-9,9-diethyl-2-fluorenyl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	216 (106,000) 291 (19,000) 362' (138,000)	407m 430 456sh	0.98
39	7,7'-Bis[7-(4- <i>t</i> -butylphenyl)-2-fluorenyl]-9,9,9',9'-tetrapropyl-2,2'-bifluorene 	216 (133,000) 260 (25,000) 366' (153,000)	413m 437 462sh	1.00
40	2,7-Bis(2-furyl)-9,9-dipropylfluorene 	209 (25,000) 231 (19,500) 346 (53,300) 364 (50,000)	377m 397 416	0.86' ⁱ 0.84 ^k
41	2,7-Bis[5-(4-methoxyphenyl)-2-furyl]-9,9-dipropylfluorene 	243 (39,000) 279 (28,300) 322 (27,900) 335 (31,000) 388 (103,000) 410 (91,000)	425m 451 481	0.79' ⁱ 0.77 ^m

^a Most intense peak, m; shoulder, sh.

^b In dioxane.

^c Insufficient sample; values determined in *N,N*-dimethylformamide; from Ref. 11.

^d Insufficient sample.

^e Insoluble in cyclohexane; value determined in *N,N*-dimethylacetamide.

^f Insoluble in cyclohexane; value determined in toluene.

^g From Ref. 10 with correction.

^h From Ref. 11 with correction.

ⁱ Wavelength used for excitation in determination of Φ_f .

^j Value when excited at 346 nm.

^k Value when excited at 364 nm.

^l Value when excited at 388 nm.

^m Value when excited at 410 nm.

RESULTS AND DISCUSSION

Limiting Absorption Wavelength. In *p*-oligophenylenes it is well-known that the single, smooth, long-wavelength absorption maximum moves to a longer

wavelength with the addition of each successive ring [4] and with each of bridge between the rings. Seliskar *et al.* defined a parameter, θ , as the sum of the number of rings plus the number of bridges in an oligophenylene

Table II. Some Photophysical Properties of Simple Oligophenylene Fluors

Compound	Fluor. em. λ max (nm) ^a	Φ_f ^b
Biphenyl	305, 316m, 325sh	0.16
Fluorene	303m, 310, 314sh	0.69
<i>N</i> -Methylcarbazole	346m, 362, 378sh	0.44
<i>p</i> -Terphenyl	325, 339m, 352sh	0.80
<i>p</i> -Quaterphenyl	349, 365m, 382sh	0.77

^a Most intense peak, m; shoulder, sh; in cyclohexane; from Ref. 4.

^b Corrected values based on $\Phi = 0.86$ for 9,10-diphenylanthracene.

and has correlated increasing molar extinction coefficients with θ [1]. In Fig. 1 a plot of $1/\theta$ against the longest-wavelength maximum absorption is shown for 25 of our oligophenylenes. Extrapolation of the best-fit line to the y axis gives a value of 386 nm for the hypothetical, "infinitely-long," fully bridged oligophenylene. This contrasts with a calculated value of 345 nm for an infinitely long oligophenylene with no bridges [26]. An earlier calculated value of 339 nm was based on an anomalously low value of ϵ reported for sexiphenyl [27].

The Quinquiphenyl Anomaly. The reported ϵ for sexiphenyl (56,000 L/mol-cm) stands in striking contrast to the abnormally high ϵ of quinquephenyl (62,500) [27]. We can revisit this anomaly by noting the almost-equal ϵ values in Table I for doubly bridged, *t*-alkyl end-capped quinquephenyls, **26** and **27**, and doubly bridged sexiphenyls, **29** and **30** (with and without *t*-alkyl end caps). The enhanced extinction coefficients of the quinquephenyls are not attributable to any structural feature, save perhaps orbital symmetry considerations.

The Effect of Alkylated Carbon Bridges on Φ_f . Unsubstituted *p*-oligophenylenes higher than quaterphenyl lack the solubility necessary for Φ_f to be measured in solution. The quinqu- to deciphenyls **26**–**39** are soluble by virtue of the disubstituted bridges between the rings. The carbon bridge is variously dialkylated by ethyl, propyl, and 2-methoxyethyl groups, the latter chosen to promote solubility in alcohols. The influence of these obligatory substituents on ϵ and Φ_f is given in Table I. The dialkylation of fluorene (Table II) to give 9,9-dipropylfluorene, **3**, reduces Φ_f substantially. The presence of the same bridging group in terphenyls (compare **7** with **9**, **8** with **10**, and **18** with **19**) decreases Φ_f slightly or not at all. With quaterphenyls or larger oligophenylenes, ethyl or propyl groups on the bridges produce no apparent diminution of Φ_f . However, the 2-methoxyethyl substituents on the bridging carbon(s) seem to cause a signif-

icant lowering of Φ_f in quaterphenyls: compare **22** and **24** with **20**, **21**, and **23**. Among quinqu- and sexiphenyls, however, compounds with 2-methoxyethylated bridges, **27**, **28**, and **32**, were not significantly different in Φ_f from the corresponding compounds with ethylated or propylated bridges, **26** and **29**–**31**. Thus in higher oligophenylenes, considerably increased solubility is obtained with only slightly diminished Φ_f .

Effects of Auxofluors. In our work with oligophenylenes as laser dyes [1,13,14] we have noted that their service lifetimes in lasing media are universally enhanced by *t*-alkyl substitution at the termini of the long axes of the fluorophores. At first we hesitated to employ such substituents because of the "loose bolt" effect [28], which diminishes Φ_f in secondary and tertiary alkyl-substituted benzenes [29,30]. This effect has been attributed to a deactivation of the excited state ($S_1 \rightarrow S_0$) through a coupling of the stretching of the $C_\alpha-C_\beta$ bonds in the alkyl group with the wave function of the excited state. The energy surface of benzene's excited (S_1) state crosses the surface of the ground (S_0) state through the mediation of the C–C bond stretching. As shown in Table I, biphenyl, fluorene, and higher oligophenylenes do not experience a diminution of Φ_f with *t*-alkyl substitution at the termini. Indeed Φ_f is frequently increased by such substitution. The reduction of Φ_f in 9,9-dipropylfluorene (**3**) compared with that of fluorene (Table II), however, may indicate that the "loose bolt" effect can operate when the *t*-alkyl substitution is found on the short axis of the molecule. As is clear from the Φ_f values in Tables I and II, the influence of dialkylated bridges diminishes as one moves on to higher oligophenylenes.

Besides *t*-alkyl, other auxofluors were placed at the termini of the oligophenylenes. The methoxy substituent, which enhances the Φ_f of benzene [4], was appended to *ter*- through sexiphenyls. Although this substitution lowered Φ_f somewhat in the smaller molecules, **8**, **10**, **12**, and **22**, the Φ_f values of the methoxy-substituted sexiphenyls were not diminished (cf. **29** with **31** and **32**). The cyclic ether auxofluors in **15**–**17** reduced Φ_f in terphenyls but raised it slightly in quaterphenyls [11].

A rarely cited publication called our attention to the value of cyano substituents in oligophenylenes for enhancing their scintillation efficiency [31]. Our measurements of three oligophenylenes terminally substituted with one or two cyano groups (**4**, **5**, and **14**) indicate that both a modest reduction in Φ_f and a substantial bathochromic shift in both the absorption and the fluorescence emission wavelengths occurred. The marked bathochromic shift of the fluorescence maximum in **5** compared with that of **3** along with the almost-negligible

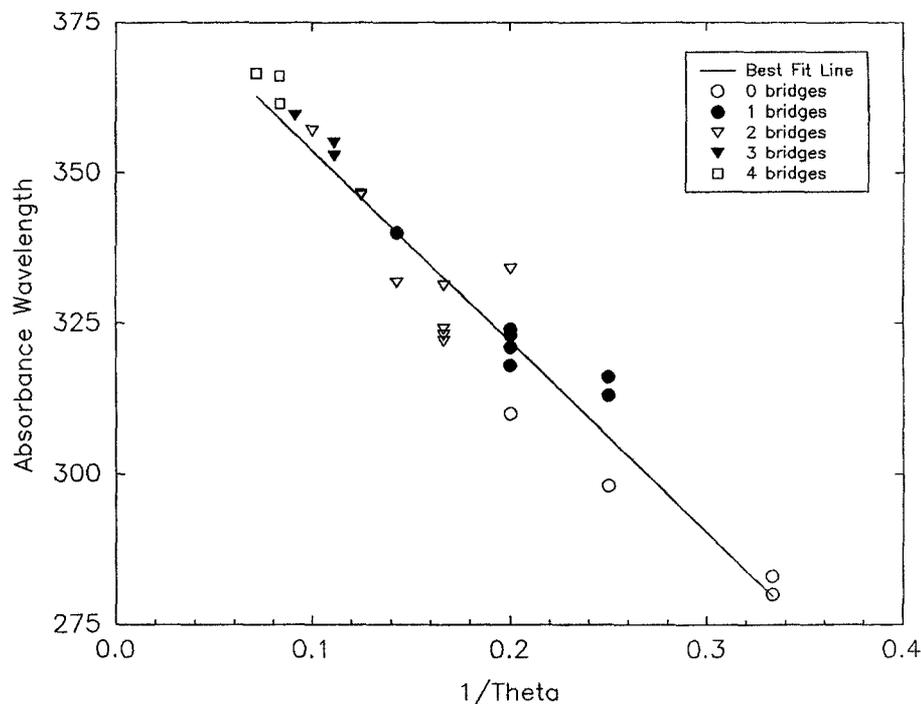


Fig. 1. Absorbance wavelength vs $1/\theta$.

diminution of Φ_f augurs well for the use of dicyano substitution in higher oligophenylenes.

Heterocyclic Fluorophores. The carbazoles **4** and **11** had lower Φ_f than the parent *N*-methylcarbazole (Table II). We had already noted a lowered Φ_f in a 2,2'-bicarbazole analogue of 2,2'-bifluorene [10].

The furans **40** and **41** were noteworthy mainly for their extreme bathochromic shifts in wavelengths from the benzene analogues **20** and **31**.

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