Novel Fluorescent Quater- and Quinquifurans: Syntheses and Photophysical Properties

Joel M. Kauffman* and Guillermo Moyna

University of the Sciences in Philadelphia (USP), 600 South 43rd St., Philadelphia, PA 19104-4495

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In the quest for fast fluors for use in waveshifting polystyrene fibers, symmetrical oligofurans were investigated. Furan moieties were coupled by means of the Ullmann Reaction or by palladium-catalyzed unsymmetrical coupling; the latter gave higher yields. While the benzoxazole-terminated quater- and quinquifurans we prepared were both stable and fast, exhibiting a green fluorescence and decay times of about 2.4 nsec, they were inferior to other types of fluors in solubility and emission intensity when incorporated into polystyrene.

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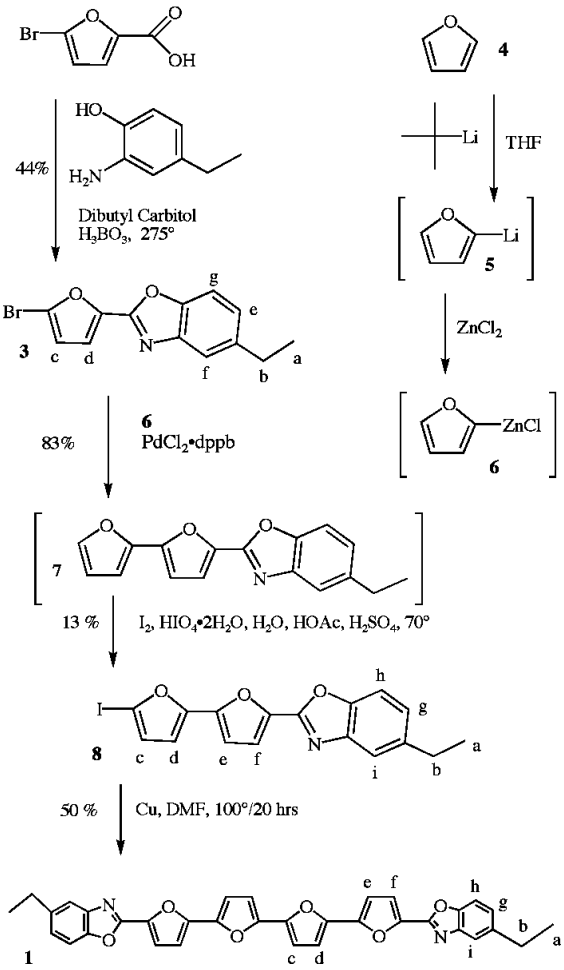
Introduction.

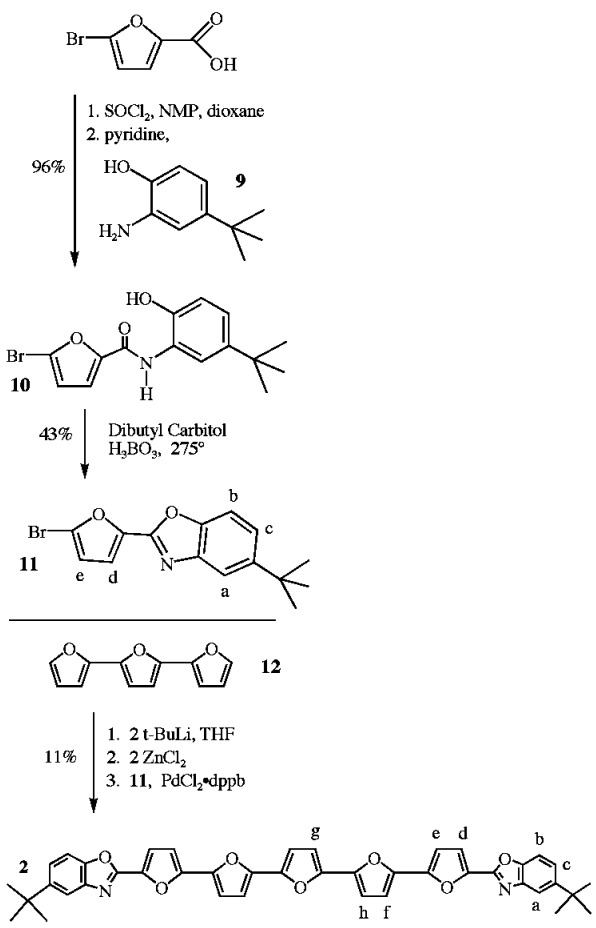
For more than a decade fluors have been sought for use as waveshifters in fiber light-guides. The plan was to collect violet-to-blue light pulses from scintillations derived from the impact of high-energy particles in polystyrene (PS) tiles by means of imbedded circular fibers, and, by means of waveshifting fluors dissolved in the fibers, to change the light emitted from the fibers to green for detection with green-sensitive photomultiplier tubes (see Figure 3a in [1]). The requirements for such waveshifting fluors have been detailed [2], and include high fluorescence quantum yield (Φ_f). Short fluorescence decay times (τ_f) have been inversely correlated with large extinction coefficients (ε) for ultraviolet absorption in oligophenylenes [3]; however, the longest practical emission wavelength obtainable, 390 nm, is from a sexiphenyl with no auxofluors [4]. Carbon-bridging of some of the rings as in an oligofluorene extends this wavelength to about 437 nm [4,5]. 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]. While the decay times for 1,6-diphenyl-1,3,5-hexatriene (12 nsec) and 1,8-diphenyl-1,3,5,7-octatetraene (6 nsec) are much too slow [7], and their photochemical stability is poor, their wavelengths were desirable; thus we thought that incorporation of the conjugated polyene system into furan rings might provide molecules with a more oligophenylene-like decay time. We had already established that benzimidazolium groups as auxofluors on a fluorene gave a bright fluor, but with too short an emission wavelength [8]. It has long been known that benzoxazoles as auxofluors on oligophenylenes or fluorenes give fluors that are photostable, bright and fast (τ_f = 1-2 nsec), albeit of far too short emission wavelength [9], so it seemed reasonable to prepare oligofurans terminated with benzoxazoles for this work. The placement of the strongly electron-attracting benzoxazol-2-yl group on the 2- and 5-positions of electron-releasing oligofurans was expected to give reasonably stable compounds. The structures of the S_1 state of symmetrical fluors terminated with benzoxazol-2-yl groups have been postulated [10]. Our earlier efforts to obtain fast fluors by extending the conjugation of unsymmetrical ones, that is, those with push-pull auxofluors, were not successful; for example, see fluor **16c** in ref. [8], and **11a-b** in ref. [11]; the molecules would not form an excited state utilizing the entire fluorophore, which, in each, encompassed only 4 aromatic rings con-

Scheme 1
Synthesis of Quaterfuran **1**



nected by single bonds. By contrast, fluors symmetrical along their long axes can display high epsilons from as many as 8 aromatic rings connected by single bonds [12]. However, such large and symmetrical molecules are also high-melting and have limited solubility. For these reasons we designed and made oligofurans **1** (Scheme 1) and **2**

Scheme 2
Synthesis of Quinquifuran **2**



(Scheme 2) with alkyl groups to provide easier purfication and higher solubility in PS.

We were unaware of any prior description of the syntheses of any quater- and quinquifurans in the peer-reviewed literature. After this work was completed, a single report of the synthesis of unsubstituted quaterfuran appeared, without detail or characterization [13].

Discussion and Results.

Syntheses.

Quaterfuran **1** (Scheme 1). Condensation of 5-bromo-2-furoic acid with 2-amino-4-ethylphenol to give **3** was carried out by an old method [14] using boric acid as catalyst in Dibutyl Carbitol™ (DBC), rather than the commonly used polyphosphoric acid, in the belief (not tested) that the furans would not survive hot aqueous acid conditions. Furan **4** was lithiated with *t*-butyllithium to give **5** and this was converted to the 2-chlorozinc, as we reported previously [11], which was coupled with **3** by means of the air-stable and under-utilized catalyst $PdCl_2$·dppb [15] to give bifuran **7** as a gum. Iodination gave a poor yield of **8**, which, at least, was well-characterized, including ^1H and ^{13}C nmr spectra. An Ullmann coupling of **8** with copper bronze gave quaterfuran **1** in good yield, whose structure is supported by a ^1H nmr spectrum and elemental assays. The coupling method reported to form plain quaterfuran from bifuran [13] would not have been applicable, since the *n*-butyllithium employed would have reacted with the C=N bond of the benzoxazole.

Quinquifuran **2** (Scheme 2). We had been successful in using Seha's method [16] for synthesis of a 2-(2-hydroxyphenyl)benzoxaxole from 2-amino-4-*t*-butylphenol **9** in one step [11], but we obtained from 5-bromo-2-furoic acid **9** mostly amide **10** . This with boric acid in DBC gave **11**. Dilithiation of the terfuran **12**, exchange to the 2,5"-di(chlorozinc), and coupling with **11** in the presence of $PdCl_2$·dppb gave quinquifuran **2**, whose structure was confirmed by 1D and 2D (COSY) ^1H nmr spectroscopy (Figure 1).

Side-chains were incorporated for greater solubility (Scheme 3). We had initially prepared a sort of lower homolog of quaterfuran **1** from 6-amino-*m*-cresol by the same method, but in very low yield, and poorly characterized. This was 6,6'''-bis(6-methyl-2-benzoxazolyl)-2,2':5',2":5",2'''-quaterfuran (**1a**; this was **22b** in ref. [17]) of mp 300-304° and $\tau_f \leq 2.5$ nsec (see Table 1). Unlike quaterfuran **1**, **1a** was too insoluble in styrene monomer for practical use, as was quinquifuran **2**. The latter, for example, was too insoluble in toluene at 20° for us to obtain UV and fluorescence spectra, which is why we used chloroform, in which the solubility was $2x10^{-7}$ *M* or 1.5 mg/L. So we prepared the intermediate **19** (Scheme 3) with a dodecyl group to enhance the solubility of the corresponding oligofurans in styrene, compared with the oligofurans derived from **3** and **11**.

There is a recent preparation of 4-dodecylphenol **16** in 40% yield by diazotization of 4-dodecylaniline [18], but the latter was far too expensive for this project. The classic method of Clemmensen reduction, when applied to 4-dodecanoylphenol, was poorly described with no yields given [19,20] and failed altogether in our hands. (In fact the prior Fries rearrangement of the phenyl ester does not give a clean 4-isomer [21]). So taking advantage of the discovery that $PdCl_2$·dppb catalyzed the coupling of methylmagnesium chloride with a 2-bromofluorene [22], we prepared from 1-bromododecane **13** the Grignard reagent **14** and coupled it with 4-iodoanisole (after finding

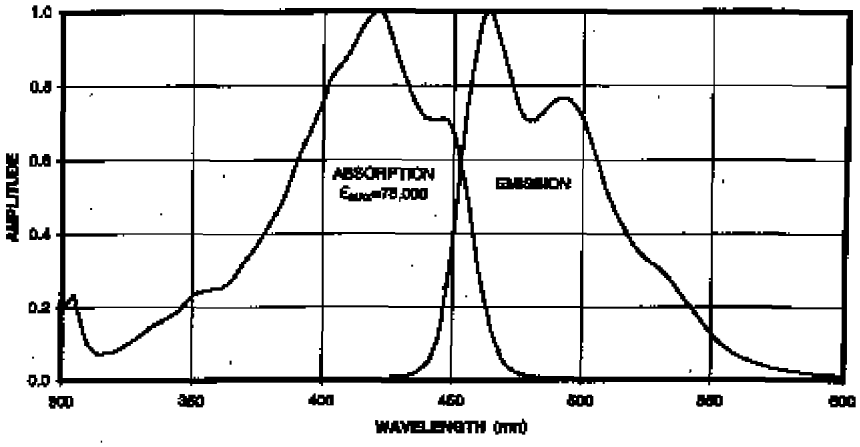
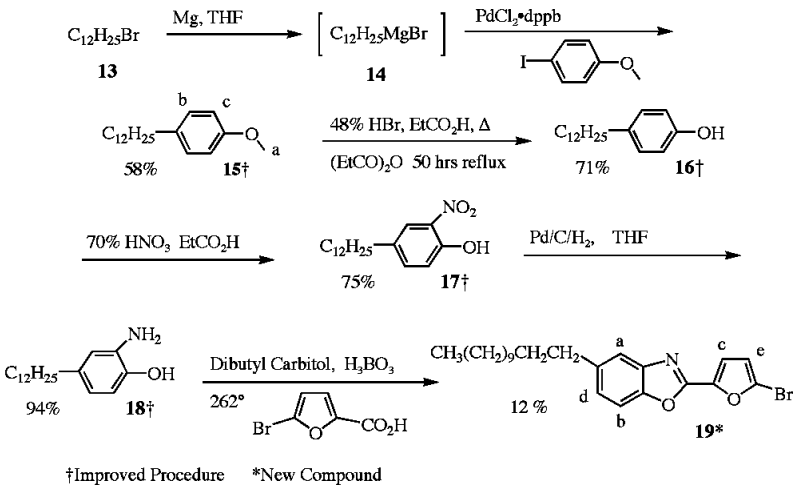


Figure 1. Optical Spectra of Quaterfuran **1** in Tolulene.

Scheme 3



†Improved Procedure *New Compound

Actual Synthesis of 4-Dodecyl-2-nitrophenol

Table 1

Absorption and Fluorescence Properties of Oligofurans and Related Tetracne

Compound	Absorption (nm) Found	(Calc) [a]	Fluorescence em. (nm) Found	(Calc) [a]	Φf	τ_f (nsee)
(E,E,E,E)-1,8-Diphenyl-1,3,5,7-octatetracne [b]	356, 373, 387	(—)	453,475,518*,556	(—)	0.08 [e]	6.2 [g]
5,5'''-Bis(5-ethyl-2-benzoxazolyl)-2,2':5',2'':5'',2'''-quaterfuran (**1**)[c]	420,444	(439)	472*,498,530	(478)	0.77 [f]	2.4 [h]
5,5''''-Bis(5-t-butyl-2-benzox-azolyl)-2,2':5',2'':5'',2''':5''',2''''-quinquifuran (2) [d]	431,455	(448)	477*, 507	(488)	0.89 [f]	2.4 [h]

[a] As described in ref. [17]; [b] From ref. [3]; [c] The calculations were for 6,6'''-Bis(6-methyl-2-benzoxazolyl)-2,2':5',2'':5'',2'''-quaterfuran, **22b** in ref. [17]; [d] Samc as **23b** in ref. [17]; [e] From [7] adjusted as in [4]; [f] Detd. in toluene as described [4] vs. DPA in toluene with $\Phi_f = 0.82$; [g] From ref. [3]; [h] The reciprocal of the slope of intensity vs. time of the fast decay component obtained by laser excitation of the sample; *Indicates the major peak.

that 4-bromoanisole was too unreactive) to give 4-dodecylanisole **15** in good yield. The classic ether cleavage with hydrobromic acid was sluggish, but use of the co-solvents propanoic acid and its anhydride, and a long reaction time gave **16** in good yield. The recently reported nitration of **16** [18] failed entirely in our hands, but the use of diluted nitric acid with the same co-solvent, propanoic acid, gave nitro **17** in good yield. Instead of the reported use of

Raney nickel for the reduction [19] we used palladium on carbon for an excellent yield of amine **18**, which, with 5-bromo-2-furoic acid, boric acid and DBC, gave a low yield of benzoxazole **19**, which was well-characterized by its ^{1}H nmr spectrum. This sequence was not carried further because the shortcomings of **1** and **2** had been recognized by this time.

Photophysical Properties.

Both quaterfuran **1** and quinquifuran **2** had fast decay times of 2.4 nsec, the fastest of any green-emitting fluors of which we are aware. No decomposition in solution at 20° was observed in contrast to plain quaterfuran, which is so unstable that spectra had to be determined on freshly prepared solutions [13]. Both **1** and **2** survived polymerization in styrene, but **1** partially precipitated on cooling because of insolubility. Both were deficient in light output compared with other fluors tested during the project because of too little Stokes' shift, not because of their quantum yields, which were high (Table 1). The extinction coefficient of **1** (77,000) was significantly lower than that of **2** (108,000), showing that the additional furan ring was contributing. This $\Delta\varepsilon$ is very large for just one additional aromatic ring. Perhaps this is due to the existence of an additional plane of symmetry in **2**, as shown by our drawings of these structures in the putative lowest-energy conformation with all oxygens *anti;* or perhaps it is due to the "quinquiphenyl effect" that has been noted [4]. The Stokes' shift of **1** was much less than that of the almost isoelectronic 1,8-diphenyl-1,3,5,7-octatetraene (Table 1); this

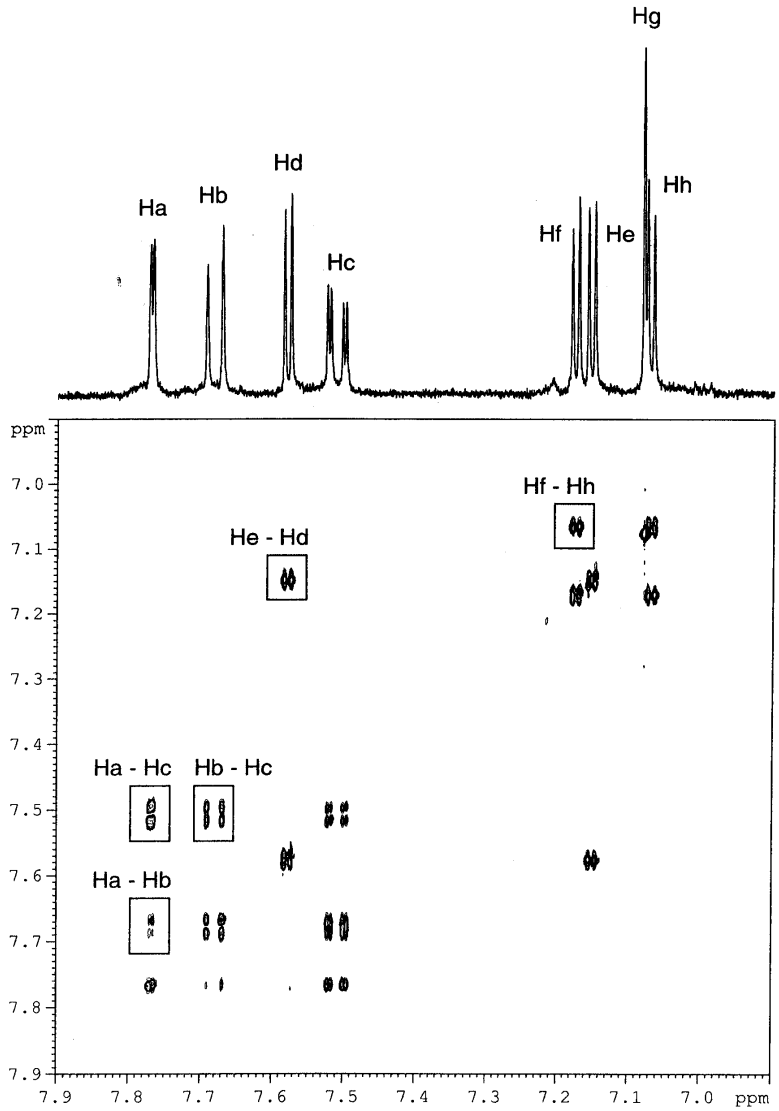


Figure 2. 1D and 2D (COSY) ^{1}H nmr spectra of compound **2**. Correlations between coupled protons are marked with boxes. See text and Scheme 2 for assignments.

means that there is much less conformational change of **1** on excitation.

Predictions of the major absorption and fluorescence wavelength peaks of **1** and **2** by computerized calculations [17] were reasonably accurate (Table 1), but the degree of self-absorption, limiting the light output of these fluors in PS, was not predicted.

EXPERIMENTAL

General.

Methods previously described [8] were followed with the exception that the 300 MHz ^{1}H nmr spectrum was determined on a Varian 300 XL, and the 400 MHz spectra on a Bruker Avance 400, and ^{13}C were recorded at 100 MHz on the latter. Lowercase letters refer to both carbon and any hydrogen attached to that carbon for nmr assignments. Dibutyl Carbitol™ (DBC) was diethylene glycol dibutyl ether, Aldrich 20,562-1. Solvents used in moisture-sensitive reactions were dried over 3A Molecular Sieve. Preparation of the catalyst palladium(II) chloride 1,4-bis(diphenylphosphino)butane ($PdCl_2$·dppb) has been described [15]. Florisil™ was Aldrich 22,074-4. Next to mp, pc means phase-change, and s means softens.

2-(5-Bromo-2-furyl)-5-ethylbenzoxazole (**3**).

With magnetic stirring, 5-bromo-2-furoic acid (80.0 g, .419 mol, Aldrich B6,740-6), 2-amino-4-ethylphenol (57.5 g, 0.419 mol, [10]), and 1.0 g of powdered boric acid in 575 mL of DBC were heated under a spray-trap/air-condenser combination, and the mixture was heated strongly to distill out water. The reaction temperature unexpectedly jumped to 275° with concurrent distillation of 500 mL of DBC and 10.5 mL of water. At 65° 500 mL of hexane was added, the liquid was decanted and cooled at -20° overnight. The sticky solid was filtered, washed with 200 mL hexane and dried at 50°/20torr/4hrs to give 87 g gummy solid, which was mixed with 100 mL of acetone, 400 mL of water and 10 g of sodium carbonate monohydrate to give a solid from which liquid was decanted. The solid was slurried with 100 mL of 1:1 methanol:water and air-dried overnight. Now no longer gummy, it was extracted from a 2-cm high column of Florisil in a large Ace-Kau with 600 mL of 1,1,2-trichlorotrifluroethane for 4 days. Solvent was distilled and recovered from the extract. The residual oil was taken up in 150 mL of 95 % ethanol, diluted with ≈ 30 mL of water to the cloud point, seeded and kept at 0° overnight. The product was filtered, washed with 100 mL of 80 % ethanol, and dried as above to give 53.3 g (44%), mp 78-79°. ^{1}H nmr: (400 MHz, DMSO-*d6*): δ 1.23 (t, 3H, J = 7.6 Hz, *Ha*), 2.74 (q, 2H, J = 7.6 Hz, *Hb*), 6.95 (d, 1H, J = 3.7, *Hc*), 7.28 (dd, 1H, J = 1.6 Hz, J = 8.3 Hz, *He*), 7.47 (d, 1H, J = 3.7 Hz, *Hd*), 7.59 (dd, 1H, J = 0.5 Hz, J = 1.6 Hz, *Hf*), 7.65 (dd, 1H, J = 0.5 Hz, J = 8.3 Hz, *Hg*); ^{13}C nmr (100 MHz, DMSO-*d6*): δ 17.0, 29.0, 111.3, 115.8, 118.0, 119.4, 142.0, 142.1, 148.7, 154.5.

Anal. Calc. for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; Br, 27.35; N, 4.80 %. Found: C, 53.60; H, 3.27; Br, 27.18; N, 4.69.

5-Ethyl-2-[5'-(2-furyl)-2-furyl]benzoxazole (**7**).

Under argon, furan (**4**, 13.1 mL, 12.25 g, 0.18 mol, Acros 11977) in 200 mL of tetrahydrofuran was cooled below 0° by means of an ice-acetone bath, then 1.5 *M t*-butyllithium in pentane (120 mL, 0.18 mol, Acros 18128) was added during 1 hour to form salt **5**; this was exothermic to the last drop. After a 2-hour period at 0° zinc chloride (24.48 g, 0.18 mol, Cerac Z-1007) was heated with a gas flame (but not fused) at 0.5 torr, allowed to cool and added to the solution of **5** in one portion. An exotherm to 35° occurred with formation of an orange color; all was soluble in 25 minutes, but was kept at 21° overnite to give **6**.

The catalyst $PdCl_2$·dppb (1.0 g, 0.0018 mol) was added, then 1/3 of a solution of 2-(5-bromo-2-furyl)-5-ethylbenzoxazole (**6**, 52.56 g, 0.18 mol) was introduced. Warm water in the bath provoked an exotherm from 35-40° with brisk reflux. The rest of the solution of **E** was added, which continued the exotherm, finally to 53°, after which the bath was heated with a hot-plate for 3 hours more of reflux. The mixture turned black in 1 hour, indicating completion of the reaction. The mixture was cooled in ice to 10° and quenched in a mixture of 500 g ice, 1 L of water and 100 mL of ethanol with propellor stirring to give a suspension that was filtered on a 12.5 cm Büchner funnel.

The filtrate in benzene was chromatographed on a 4.5 cm diam. 30 cm high column of alumina using 1.2 L of benzene to obtain, after evaporation, 41.7 g (83 % crude) of viscous oil (**7**), which did not crystallize even after 1 year. Tlc on Whatman MK6F Silica Gel with toluene showed the same R_f = 0.28 as **3**. On Analtech Alumina GF, toluene, **3** had R_f = 0.73, a non-fluorescent spot that turned brown; while **7** had R_f = 0.63 with a powerful violet fluorescence under longwave uv. The structure of **7** was confirmed by its conversion to **8** below.

5-Ethyl-2-[5'-(5"-iodo-2-furyl)-2-furyl]benzoxazole (**8**).

The 5-ethyl-2-[5'-(2-furyl)-2-furyl]benzoxazole (**7**, 41.0 g, 0.147 mol) was dissolved in 300 mL of acetic acid with magnetic stirring. Then 4.5 mL of sulfuric acid diluted first with 30 mL of water was added, and the whole warmed to 45° on a mantle. A mixture of iodine (15.0 g, 0.0589 mol, Fisher I-37) and periodic acid (7.18 g, 0.0315 mol, Fisher A-223) was ground in a mortar, then ≈ 10 % was added to the solution of **7** at 45°, then another 10 % every 10 minutes, at 55°, then at 65°, then at 70° thereafter. The reaction seemed to stop when ≈ 70 % had been added, and under long UV a weak blue-green fluorescence replaced a powerful violet fluorescence, all during an additional 1-hour period at 70°. The product mixture was decanted from ≈ 5 g of gum into 600 mL each of ice and water to give a granular precipitate, which was filtered, washed with 300 mL of 95 % ethanol and air-dried overnight, becoming gummy in the process.

The gum was fractionally crystallized from methanol-acetone mixtures at -20° in several portions to give about 13 g of which the largest fraction had mp 128-133°. This orange solid was extracted from a 4-cm high column of Florisil in a medium Ace-Kau with 250 mL of cyclohexane. The extract at 21° was decanted from the pure product, which was dried at 80°/20 torr/1hr to give 7.68 g (13 %) of rust-colored needles of **8**, mp 139-141°; ^{1}H nmr (400 MHz, DMSO-*d6*): δ 1.24 (t, 3H, J = 7.6 Hz, *Ha*), 2.74 (q, 2H, J = 7.6 Hz, *Hb*), 6.92 (d, 1H, J = 3.6 Hz, *Hc*), 6.94 (d, 1H, J =3.6 Hz, Hd), 7.03 (d, 1H, J = 3.8 Hz, He), 7.28 (dd, 1H, J = 1.6 Hz, J = 8.3 Hz, Hg), 7.53 (d, 1H, J = 3.8 Hz, *Hf*), 7.60 (dd, 1H, J = 0.5 Hz, J = 1.6 HHz, *Hh*), 7.67 (dd, 1H, J = 0.5 Hz, J = 8.3 Hz, *Hi*); ^{13}C nmr (100 MHz, DMSO-*d6*): δ 17.0, 29.0, 95.1, 109.4, 111.3, 111.8, 117.6, 119.3, 123.3, 126.5, 141.8, 142.1, 142.3, 148.1, 148.9, 150.0, 155.2.

Anal. Calc. for $C_{17}H_{12}INO_3$: C, 50.39; H, 2.99; I, 31.32; N, 3.46 %. Found: C, 50.32; H, 2.99; I, 31.19; N, 3.37.

5,5'''-Bis(5-ethyl-2-benzoxazolyl)-2,2':5',2'':5'',2'''-quaterfuran (**1**).

Copper bronze (3.20 g, 0.0500 mol, Aldrich 29,258.3) and 5-ethyl-2-[5'-(5''-iodo-2-furyl)-2-furyl]benzoxazole (**8**, 7.30 g, 0.0180 mol) in 75 mL of dry *N*,*N*-dimethylformamide was heated with rapid magnetic stirring at 80°/18 hours, then at reflux (151°) for 1 hour. At 21° the solids were filtered, washed with 50 mL of acetone, and dried at 100°/20torr/1hour to give 8.6 g, which was extracted from a 2-cm high column of Florisil in a medium Ace-Kau with 125 mL of tetrahydrofuran for 2 days to give a total of 2.85 g (57 %) of orange-yellow microneedles, all of which was extracted again in the same manner for 18 hours to give 2.48 g (50%), mp 285-286.5°; uv (toluene, $2.3x10^{-5}$ *M*): 420 nm (77,000), 444 (55,000); fluorescence emission of same solution: 472 (79 rel int), 498 (100), 530 sh (57), see Figure 1; τ_f = 2.4 nsec; ^{1}H nmr (400 MHz, satd. in DMSO-*d6* at 70°): δ 1.28 (t, 3H, J = 7.5 Hz, *Ha*), 2.78 (q, 2H, J = 7.5 Hz, *Hb*), 7.09 (d, 1H, J = 3.8 Hz, *Hc*), 7.15 (d, 1H, J = 3.7 Hz, *He*), 7.17 (d, 1H, J = 3.8 Hz, *Hd*), 7.31 (dd, 1H, J = 1.6 Hz, J = 8.3 Hz, *Hg*), 7.57 (d, 1H, J = 3.7 Hz, *Hf*), 7.62 (d, 1H, J = 1.6 Hz, *Hi)*, 7.68 (d, 1H, J = 8.3 Hz, *Hh*).

Anal. Calc. for $C_{34}H_{24}N_2O_6$: C, 73.37; H, 4.35; N, 5.03 %. Found: C, 73.12; H, 4.36;N, 4.98.

N-(2-hydroxy-5-*t*-butylphenyl)-5-bromofuran-2-carboxamide (**10**).

Under argon a mixture of 5-bromo-2-furoic acid (19.1 g, 0.100 mol, Acros 10702), 100 mL of dioxane, thionyl chloride (10.9 mL, 17.85 g, 0.150 mol, Aldrich 23,046-4), and 1 mL of *N*-methylpyrrolidinone were heated to reflux, which began at 98°, and increased over 1.75 hours to 104°, after which 20 mL of dioxane was distilled out to remove the excess thionyl chloride from the acid chloride.

Separately, under argon, a solution of 2-amino-4-*t*-butylphenol (**9**, 16.5 g, 0.100 mol, Acros 18583), pyridine (8.5 mL, 8.31 g, 0.105 mol) and 75 mL of dioxane was treated with the acid chloride solution above below 28°. The mixture was kept for 3 days, diluted with 20 mL of water, then quenched in 500 mL of water. The solid product was collected, washed with 50% methanol, then slurried in 200 mL of the same for 10 minutes, and filtered, and dried at 100°/30 torr/2 hours to give 32.32 g (96%), mp 203-206°; ir (2% in $CHCl_3$): 3600-2400 (br, intra-bonded O-H), 3400 (N-H str), 3000 w, 2958 (-CH_3), 2900 w, 2865 w, 1710, 1642 (C=O), 1600, 1587, 1528, 1503, 1467, 1313, 1243, 1200, 1112, 1010 cm^{-1}.

The structure of **10** was confirmed by its conversion to **11** below.

2-(5-Bromo-2-furyl)-5-*t*-butylbenzoxazole (**11**).

With magnetic stirring, *N*-(2-hydroxy-5-t-butylphenyl)-5-bromofuran-2-carboxamide (**10**, 9.07 g, 0.0268 mol) and 0.20 g of powdered boric acid in 75 mL of DBC were heated strongly under a spray-trap/air-condenser combination to distill out water. After allowing this to cool, most of the DBC was removed by distillation at 96°/0.7 torr. The residue was covered with 50 mL of methanol and kept at -20° overnight to give 5.66 g of **11**, mp 98-100°, which was extracted from 4 cm of Silica Gel in a medium Ace-Kau with 200 mL of 1,1,2-trichlorotrifluroethane. The extract was evaporated and the residue recrystallized from 50 mL of methanol at -20° to give tan spars, mp 100-103°, 3.73 g (43%). This was extracted from 2 cm each basic and neutral alumina in a medium Ace-Kau with 75 mL of 1,1,2-trichlorotrifluroethane to give 3.2 g (37%), mp 102-103°.

Anal. Calc. for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.38 %. Found: C, 56.66; H, 4.73; N, 4.76.

Because of a peculiarity in the ^{1}H nmr spectrum, the above material was further purified by extraction from Merck 10181 Silica Gel in an Ace-Kau with hexanes. The extract was kept at -20° to give two fractions. The latter, mp 103-105°, showed ^{1}H nmr (major conformer, 400 MHz, DMSO-*d6*): δ 1.35 (s, 9H, (C*H*3)3-C-), 6.86 (d, 1H, J = 3.7 Hz, *He*), 7.49 (dd, 1H, J = 1.8 Hz, J = 8.6 Hz, *Hc*), 7.51 (d, 1H, J = 3.7 Hz, *Hd*), 7.65 (dd, 1H, J = 0.5 Hz, J = 8.6 Hz, *Hb*), 7.74 (dd, 1H, J = 0.5 Hz, 1.8 Hz, *Ha*).

2,2':5',2''-Terfuran (**12**).

Some 1,4-di(2-furyl)-1,4-butanedione was prepared as described from furfural and divinylsulfone by the method of El-Hajj [23] in 18% yield, mp 130-133°. It was not clear which catalyst had been used; we chose 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide, Aldrich 33,124-4. The terfuran **12** was obtained from the dione by the method of Asano [24] in 52% yield, mp 59-63°; this was raised to 64-65° after extraction of the crude from Merck 10181 Silica Gel in an Ace-Kau with 1,1,2-trichlorotrifluoroethane (lit. 62-63° [24]).

5,5''''-Bis(5-*t*-butyl-2-benzoxazolyl)-2,2':5',2'':5'',2''':5''',2''''-quinquifuran (**2**).

First, terfuran (**12**, 3.00 g, 0.015 mol) in 200 mL of tetrahydrofuran was cooled to -5°, then 1.5 *M t*-butyllithium in pentane (20 mL, 0.030 mol, Acros 18128) was added below 0°. The dilithium derivative separated and the suspension was kept in ice for 2.15 hours before the addition of solid, fused, anhydrous zinc chloride (4.10 g, 0.030 mol, Cerac). The exotherm to 6° was followed by heating to 30° during 30 minutes. Then 2-(5-bromo-2-furyl)-5-t-butylbenzoxazole (**11**, 9.6 g, 0.030 mol) was added, then $PdCl_2$·dppb (0.30 g, 0.005 mol). The reactor was moved to a mantle and heated, to cause an exotherm to reflux at 57°; heat was stopped, 200 mL of methanol was added, and the mixture was stirred overnight. The precipitated yellow solid was collected, washed with methanol and dried to give 7.43 g of orange solid, mp pc 310-320°, 335-337° dec. This solid was extracted from a soxhlet with 200 mL of tetrahydrofuran. The extract was kept at 20° overnight, collected, washed with acetone, and dried to yield 1.58 g, which was extracted from 1 cm of 35-70 mesh Silica Gel in a small Ace-Kau with 3-chlorotoluene to give a total of 1.5 g (15%) of **2**, mp 341-344°; uv ($2.2x10^{-7}$ *M* in $CHCl_3$): 431 nm (108,000), 455 sh (80,000); fluorescence emission of same solution: 477 nm (100), 507 (80); τ_f = 2.4 nsec; ^{1}H nmr (400 MHz, satd. in DMSO-*d6* at 70°): δ 1.38 (s, 18H, (C*H*3)3C-), 7.07 (d, 1H, J = 3.8 Hz, *Hh*), 7.08 (s, 1H, *Hg*), 7.15 (d, 1H, J = 3.7 Hz, *He*), 7.17 (dd, 1H, J = 3.8 Hz, *Hf*), 7.50 (dd, 1H, J = 1.8 Hz, 8.7 Hz, *Hc*), 7.57 (d, 1H, J = 3.7 Hz, *Hd*), 7.68 (dd, 1H, J = 0.6 Hz, J= 8.7 Hz, *Hb*), 7.77 (dd, 1H, J = 0.6 Hz, J = 1.8 Hz, *Ha*); see Fig. 2.

Anal. Calc. for $C_{42}H_{34}N_2O_7$: C, 74.32; H, 5.05; N, 4.13 %. Found: C, 74.11; H, 5.16; N, 4.19.

4-Dodecylanisole (**15**).

From 1-bromododecane (**13**, 123 mL, 127 g, 0.513 mol, Acros 10691) and magnesium (12.48 g, 0.513 mol, Reade RMC-3) in 1.5 L of tetrahydrofuran, the dodecylmagnesium bromide **14** was prepared; this involved a 1-hour addition of **13** and 2.5 hours of reflux. When the mixture cooled down to 62°, $PdCl_2$·dppb (3.1 g, 0.00513 mol) was added, followed by 4-iodoanisole (90.0 g, 0.385 mol) in multi-gram portions. A mild exotherm from

66-69° to reflux was noted, and reflux was maintained overnight. Separately a solution of ammonium chloride (8.0 g, 0.15 mol) in 25 mL of water was added at 44°; this caused an exotherm to 52°. After 3 days at 20° the liquid was decanted, evaporated, evaporated again with 300 mL of toluene, the residual oil taken up in 300 mL of hexane, some solid removed, the hexane evaporated, and the product distilled at 175-195°/0.45 torr to give 61.4 g (58%) of **15**, fp 23°; ^{1}H nmr (2.5% in DMSO-d_6, 400 MHz): δ 0.86 (t, 3H, J = 7.0 Hz, C*H*3(CH2)9CH2CH2-), 1.24 (m, 18H, CH3(C*H*2)9CH2CH2-) 1.51 (m, 2H, 2H, CH3(CH2)9C*H*2CH2-), 2.49 (t, 2H, J = 7.6 Hz, CH3(CH2)9CH2C*H*2-), 3.71 (s, 3H, *Ha*), 6.82 (AA'XX', 2H, *Hb*), 7.08 (AA'XX', 2H, *Hc*); ^{13}C NMR (100 MHz, 2.5% in DMSO-*d6*): δ 14.8, 22.9, 29.4, 29.6, 29.7, 29.8, 29.9, 32.1, 32.2, 35.1, 114.5, 129.9, 135.0, 158.1. The structure of **15** was further confirmed by its conversion to **16**, **17** and **18** below.

4-Dodecylphenol (**16**).

A mixture of 4-dodecylanisole (**15**, 61.3 g, 0.222 mol) with 150 mL of 48% hydrobromic acid and 135 mL of propanoic acid was boiled under reflux for 6 hours, then cooled to -20°; the solid was isolated by decantation, triturated with 150 mL of cold 50% methanol, filtered and air-dried. This was subjected to the acid treatment again; but, because the initial reflux temperature was only 117°, 50 mL was distilled out, then 22 mL of propanoic anhydride was added, and the mixture was boiled under reflux (119°) for 50 hours. At 40° the upper organic layer was diluted with an equal volume of methanol and held at -20° to crystallize the product, 68 g, mp s. 40°, 55-62°. This was recrystallized from 300 mL of methanol at -20° to give white plates, 41.2 g (71%), mp s. 55°, 66-68°, (lit. mp 64-65° [20], 40%, mp 65° [18]).

4-Dodecyl-2-nitrophenol (**17**).

Nitration of 4-dodecylphenol (**16**, 30.0 g, 0.109 mol) was accomplished by suspending it in 200 mL of propanoic acid and adding a mixture of 20 mL each of 70% nitric acid and water below 5°, and stirring for an hour at 5°. The resulting homogeneous mixture was diluted with 600 mL of water and extracted with 300 mL of ether. The extract in 1200 mL of water was treated with excess sodium bicarbonate, separated, washed with 200 mL of water, dried over magnesium sulfate, and evaporated to give 51 g of orange solid, which was recrystallized from 200 mL of pentane at -20° to give 26.2 g (75%), mp 53-55°; (lit. mp 55-56° [19], 82%, mp 54° [18]).

2-Amino-4-dodecylphenol (**18**).

Reduction in a Parr hydrogenator beginning with 50 psig hydrogen pressure was carried out on 4-dodecyl-2-nitrophenol (**17**, 31.9 g, 0.100 mol) in 800 mL of tetrahydrofuran with 13.2 g of recovered 10% Pd/C catalyst overnight. After removal of the catalyst and solvent, the tan plates were recrystallized from 150 mL of methanol at -20° to give 27.2 g (94%), mp s. 105°, 119-126°; (lit. 125-126° [19]).

2-(5-Bromo-2-furyl)-6-dodecylbenzoxazole (**19**).

The method used for **11** was applied to 5-bromo-2-furoic acid and **18** to give a solid (crude **19**) from methanol. This in hexane was passed through alumina, followed by more hexane to give an eluate, which was evaporated, and the residual oil was recrystallized from ethanol at -20° to give 21%, mp 57-61°. This was chromatographed on Merck 10181 Silica Gel with cyclohexane and benzene to give an oil which was crystallized from ethanol at -20°, then twice from 1,1,2-trichlorotrifluoroethane at -20° to give 3.76 g (12%), mp 64.5-66°; ^{1}H nmr (10% in CCl_4, 300 MHz): δ = 0.90 (t, 3H, J = 5 Hz, C*H*$_3$(CH$_2$)$_9$CH$_2$CH$_2$-); 1.31 (m, 18H, CH$_3$(C*H*$_2$)$_9$CH$_2$CH$_2$-); 1.68 (m, 2H, CH$_3$(CH$_2$)$_9$C*H*$_2$CH$_2$-); 2.73 (t, 2H, J = 5 Hz, CH$_3$(CH$_2$)$_9$CH$_2$C*H*$_2$-); 6.549 (d, 1H, J = 3.6 Hz, *He*); 7.168 (1H, dd, J = 0.6, 8.2 Hz, *Hd*); 7.185 (1H, d, J = 3.6 Hz, *Hc*); 7.434 (1H, d, J = 8.2 Hz, *Hb*); 7.534 (1H, d, J = 0.6 Hz, *Ha*).

Anal. Calc. for C$_{23}$H$_{30}$BrNO$_2$: C, 63.89; H, 6.99; N, 3.24 %. Found: C, 64.43; H, 6.61; N, 3.43.

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