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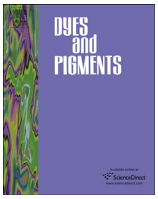

Synthesis and photoluminescent properties of conjugated aryl–vinyl dioctyl 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate derivatives

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ABSTRACT

The synthesis of highly fluorescent conjugated benzodifuran aryl–vinyl systems, containing four double bonds and at least four phenyl rings, is described. The ethyl groups of diethyl 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate, obtained by the Michael type condensation of *p*-benzoquinone and ethyl acetoacetate, were replaced by octyl groups via the transesterification reaction to improve the desired product solubility in common organic solvents. The dioctyl ester was brominated and used for the Wittig reaction with stilbene aldehydes, obtained by the Heck reaction of 4-bromobenzaldehyde and an appropriate styrene. The products, obtained in 48–92% yield, exhibit the UV–Vis fluorescence with high quantum yields, 58–69%.

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1. Introduction

Fluorescent compounds have attracted much interest because of their potential applications in flat panel displays [1–4] and solid state lighting [5–8]. The main advantages of organic light-emitting diodes (OLEDs) based on fluorescent materials are their low-power consumption, high brightness and high contrast of full color flat panel displays. Among the small molecule fluorescent materials, the most efficient emitters are distyrylarylenes [9–18] and oligophenyl vinyl compounds [19–24]. Benzodifuran (**BDF**) derivatives, due to their fluorescent properties, represent an important and little explored group of heterocyclic compounds that can be used for OLED applications. Recently, the first examples of benzodifuran small molecule materials [25–32], and polymers [33,34] have been reported. We also described aryl–vinyl benzodifuran systems of excellent fluorescent quantum yields [35,36]. Herein, the synthesis and fluorescence characterization of highly fluorescent benzodifurans containing an extended aryl–vinyl system are described.

2. Experimental

2.1. Materials and general methods

Experiments with air and moisture sensitive materials were carried under argon atmosphere. Glassware was oven dried for several hours, assembled hot, and cooled in a stream of argon. Silica gel 60, Merck 230–400 mesh, was used for preparative column flash chromatography. Analytical TLC was performed using Merck TLC Silica gel 60 F_{254} 0.2 mm plates. Reagents were commercially available from Sigma–Aldrich, Merck or Fluorochem and were used without further purification. Diethyl 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate (**2**) [35] and montmorillonite-supported $PdCl_2$ catalyst [37] were prepared according to literature procedures. Solvents were purchased from POCh Gliwice, Poland and Sigma–Aldrich. Toluene and *p*-xylene were distilled from sodium benzophenone ketyl prior to use, carbon tetrachloride, dichloromethane, chloroform, diethyl ether, and 2-propanol were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz or Bruker Advance III 700 MHz instrument at ambient temperature. Chemical shifts are reported in parts per million (δ scale), coupling constants (J values) are listed in

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Hertz. IR spectra were recorded on Mattson FTIR Genesis II spectrometer with ATR attachment. Melting points were determined with a Büchi SMP 32 and Barnstead-Thermolyne Mel-Temp II apparatus in open capillaries and are uncorrected. Elemental analyses were performed at Elementary Analysensysteme GmbH VarioMACRO CHN analyzer.

2.1.1. Spectroscopic measurements

Dichloromethane (spectrometric grade from Aldrich) was employed as solvent for absorption and fluorescence measurements. UV/Vis absorption spectra were recorded on a UNICAM Helios-α spectrophotometer in a 1-cm quartz cell, in comparison to solvent blank. Emission spectra were obtained on a Hitachi F-7000 Fluorescence Spectrophotometer and on a JASCO FP-8500 spectrometer. The quantum yield was determined using fluorescein in 0.1 M NaOH as reference. Excitation wavelength for all materials was 460 nm. The concentration of fluorescein and the analyzed substances were set in a way that the absorbance at 460 nm was low enough to avoid the inner filter effect. A reference value of 0.9 for the fluorescein quantum yield was used. The fluorescence lifetime was determined using a time-correlated single-photon counting setup with a Maestro spectrum analyzer (EG&G Ortec, Oak Ridge, USA) and a pulsed LED (376 nm, PicoQuant GmbH, Berlin, Germany) with a pulse width of less than 1.5 ns (FWHM). All fluorescence light above 406 nm was detected using a low-pass filter. The decay traces were analyzed assuming a single exponential decay function.

2.2. Synthesis of the compounds

2.2.1. Dioctyl 2,6-dimethylbenzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (3)

2,6-Dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate (**2**) (16.52 g, 50.0 mmol), 1-octanol (150 mL), anhydrous potassium phosphate (10.61 g, 50.0 mmol) and *tert*-butylammonium bromide (2.0 g, 6.2 mmol) were refluxed in Dean–Stark apparatus for 9 h. The mixture was cooled to room temperature, dichloromethane (200 mL) and water (400 mL) were added and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL), combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed on a rotary evaporator. Methanol (200 mL) was added and the mixture was left at −20 °C for 16 h. The precipitated product was filtered and crystallized from methanol: ethyl acetate (1:1), yielding 19.45 g (78%), of white powder. mp = 84–86 °C. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 0.87 (t, J = 7.0 Hz, 6H, 2 × CH$_3$), 1.25–1.33 (m, 12H, 6 × CH$_2$), 1.34–1.39 (m, 4H, 2 × CH$_2$), 1.45–1.49 (m, 4H, 2 × CH$_2$), 1.81 (dt, J = 14.7 Hz, J = 7.0 Hz, 4H, 2 × CH$_2$), 2.78 (s, 6H, 2 × CH$_3$), 4.35 (t, J = 7.0 Hz, 4H, 2 × CH$_2$), 7.93 (s, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 175 MHz); δ ppm: 14.07 (2 × CH$_3$), 14.74 (2 × CH$_3$), 22.64 (2 × CH$_2$), 26.15 (2 × CH$_2$), 28.81 (2 × CH$_2$), 29.18 (2 × CH$_2$), 29.24 (2 × CH$_2$), 31.78 (2 × CH$_2$), 65.54 (2 × CH$_2$), 102.81 (2 × CH), 109.14 (2 × C), 123.92 (2 × C), 151.20 (2 × C), 164.51 (2 × C), 164.57 (2 × C). IR (ATR) ν_{max} cm^{-1}: 2953, 2923, 2853, 1709, 1674, 1599, 1422, 1399, 1337, 1255, 1181, 1148, 1073, 1003, 961, 857, 801, 781, 706, 634. Anal. Calcd. for $C_{30}H_{42}O_6$: C, 72.26; H, 8.49. Found: C, 72.54; H, 8.52.

2.2.2. Dioctyl 2,6-bis(bromomethyl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (4)

To a solution of **3** (18.43 g, 35 mmol) in carbon tetrachloride (250 mL), *N*-bromosuccinimide (7.46 g, 41.8 mmol) and AIBN (0.5 g) were added and the mixture was refluxed for 4 h. Another portion of *N*-bromosuccinimide (7.46 g, 41.8 mmol) and AIBN (0.5 g) were added and the mixture was stirred under reflux for an additional 20 h. Most of the carbon tetrachloride (200 mL) was distilled off, methanol (200 mL) was added and the mixture was cooled to −20 °C, and left at this temperature for 72 h. The yellow precipitate was collected by filtration and crystallized from chloroform: methanol (3:2) to afford **4** (13.33 g, 58%) as a pale yellow solid. mp = 132–136 °C. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 0.87 (t, J = 7.0 Hz, 6H, 2 × CH$_3$), 1.26–1.35 (m, 12H, 6 × CH$_2$), 1.36–1.40 (m, 4H, 2 × CH$_2$), 1.46–1.51 (m, 4H, 2 × CH$_2$), 1.84 (dt, J = 15.4 Hz, J = 7.0 Hz, 4H, 2 × CH$_2$), 4.40 (t, J = 7.0 Hz, 4H, 2 × CH$_2$), 4.98 (s, 4H, 2 × CH$_2$), 8.08 (s, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 14.03 (2 × CH$_3$), 21.25 (2 × CH$_2$), 22.61 (2 × CH$_2$), 26.10 (2 × CH$_2$), 28.68 (2 × CH$_2$), 29.15 (2 × CH$_2$), 29.21 (2 × CH$_2$), 31.75 (2 × CH$_2$), 65.32 (2 × CH$_2$), 104.33 (2 × CH), 111.10 (2 × C), 124.84 (2 × C), 151.84 (2 × C), 160.48 (2 × C), 163.14 (2 × C). IR (ATR)ν_{max} cm^{-1}: 2951, 2920, 2850, 1707, 1596, 1464, 1420, 1397, 1351, 1259, 1186, 1086, 1050, 935, 880, 826, 786, 722, 703. Anal. Calcd. for $C_{30}H_{40}Br_2O_6$: C, 54.89; H, 6.14. Found: C, 55.12; H, 6.11.

2.2.3. (3,7-Bis(octyloxycarbonyl)benzofuro[5,6-b]furan-2,6-diyl) bis(methylene)bis(triphenylphosphonium) bromide (5)

Dioctyl 2,6-bis(bromomethyl)benzo[1,2-*b*:4,5-*b*′]difuran-3,7-dicarboxylate (**4**) (12.47 g, 19.0 mmol) and triphenylphosphine (14.93 g, 57.0 mmol) were refluxed in toluene (200 mL) for 30 min. The mixture was cooled to room temperature, precipitated salt was collected by filtration, washed with diethyl ether (4 × 60 mL) and dried in vacuum to afford **5** (22.30 g, 99%) as a green-yellow powder. mp = 88–90 °C. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 0.88 (t, J = 7.0 Hz, 6H, 2 × CH$_3$), 1.28–1.32 (m, 20H, 10 × CH$_2$), 1.64 (t, J = 7.0 Hz, 4H, 2 × CH$_2$), 4.09 (t, J = 7.0 Hz, 4H, 2 × CH$_2$), 6.49 (d, J = 15.4 Hz, 4H, 2 × CH$_2$), 7.59–7.61 (m, 14H, 14 × CH$_{Ar}$), 7.74 (t, J = 7.0 Hz, 6H, 6 × CH$_{Ar}$), 7.82–7.86 (m, 12H, 12 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 14.12 (2 × CH$_3$), 22.64 (2 × CH$_2$), 25.87 (2 × CH$_2$), 26.43 (2 × CH$_2$), 28.55 (2 × CH$_2$), 29.13 (2 × CH$_2$), 29.17 (2 × CH$_2$), 31.82 (2 × CH$_2$), 65.31 (2 × CH$_2$), 104.18 (2 × CH), 113.60 (C), 113.68 (C), 117.20 (2 × C), 117.70 (2 × C), 123.35 (2 × C), 130.11 (6 × CH), 130.25 (6 × CH), 134.06 (6 × CH), 134.17 (6 × CH), 135.24 (6 × CH), 151.71 (2 × C), 154.79 (2 × C), 154.91 (2 × C), 163.03 (2 × C). 2953, 2924, 2852, 1709, 1676, 1599, 1435, 1425, 1398, 1256, 1181, 1148, 1107, 1073, 1055, 997, 961, 858, 782, 742, 728, 705, 687. Anal. Calcd. for $C_{66}H_{70}Br_2O_6P_2$: C, 67.12; H, 5.97. Found: C, 66.71; H, 5.92.

2.3. General procedure for styrenes

A mixture of methyltriphenylphosphonium iodide (20.0 mmol) in dry THF (150 mL) was cooled to −78 °C and *n*-butyllithium (2.5 M in hexanes) (8 mL, 20.0 mmol) was added dropwise. The mixture was allowed to worm to room temperature, stirred for additional 30 min and cooled again to −78 °C. Aldehyde (20.0 mmol) in THF (10 mL) was added dropwise, mixture was allowed to worm to room temperature and stirred at this temperature for 2 h. Resulting precipitate was filtered off on a sintered funnel, TBME (350 mL) was added to the filtrate, and the mixture was stirred for additional 10 min and filtered again. The solvent was removed on rotary evaporator and the product was purified by flash chromatography.

2.3.1. 1-Fluoro-4-vinylbenzene

Prepared from 4-fluorobenzaldehyde and purified by flash chromatography, acetone: petroleum ether (2:8). Pale yellow oil, 56%. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 5.18–5.21 (m, 1H, CH), 5.62–5.67 (m, 1H, CH), 6.66 (dd, J = 10.8 Hz, J = 17.2 Hz, 1H, CH), 6.97–7.01 (m, 2H, 2 × CH$_{Ar}$), 7.33–7.37 (m, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 113.50 (CH$_2$), 115.28 (CH), 115.49 (CH), 127.68 (CH), 127.76 (CH), 132.91 (C), 135.68 (CH), 161.23 (C).

2.3.2. 1-Nitro-4-vinylbenzene

Prepared from 4-nitrobenzaldehyde and purified by flash chromatography, ethyl acetate: petroleum ether (1:1). Colorless oil, 46%. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 5.47 (d, J = 11.2 Hz, 1H, CH), 5.90 (dd, J = 17.6 Hz, J = 0.8 Hz, 1H, CH), 6.75 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H, CH), 7.49–7.52 (m, 2H, 2 × CH$_{Ar}$), 8.14–8.17 (m, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 119.58 (CH$_2$), 124.95 (2 × CH), 127.81 (2 × CH), 135.99 (CH), 144.82 (C), 148.21 (C).

2.3.3. 1-(Trifluoromethyl)-4-vinylbenzene

Prepared from 4-(trifluoromethyl)benzaldehyde and purified by flash chromatography, acetone: petroleum ether (2:8). Pale yellow oil, 37%. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 5.37 (d, J = 10.5 Hz, 1H, CH), 5.83 (d, J = 17.5 Hz, 1H, CH), 6.73 (dd, J = 10.5 Hz, J = 17.5 Hz, 1H, CH), 7.48 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.56 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 175 MHz); δ ppm: 116.54 (CH$_2$), 122.44 (C), 125.55 (CH), 125.65 (CH), 126.48 (2 × CH), 129.74 (C), 135.72 (CH), 141.02 (C).

2.3.4. 1,2,3-Trimethoxy-5-vinylbenzene

Prepared from 3,4,5-trimethoxybenzaldehyde and purified by flash chromatography, acetone: petroleum ether (1:9). Colorless oil, 59%. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 3.83 (s, 3H, CH$_3$), 3.86 (s, 6H, 2 × CH$_3$), 5.19 (d, J = 10.5 Hz, 1H, CH), 5.64 (dd, J = 17.5 Hz, J = 0.7 Hz, 1H, CH), 6.62 (dd, J = 17.5 Hz, J = 10.5 Hz, 1H, CH), 6.62 (s, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 175 MHz); δ ppm: 55.93 (2 × CH$_3$), 60.75 (CH$_3$), 103.12 (2 × CH), 113.16 (CH$_2$), 133.29 (C), 136.63 (CH), 137.94 (C), 153.21 (2 × C).

2.3.5. Methyl(4-vinylphenyl)sulfane

Prepared from 4-(methylthio)benzaldehyde and purified by flash chromatography, acetone: petroleum ether (2:8). Colorless oil, 42%. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 2.47 (s, 3H, CH$_3$), 5.19 (dd, J = 10.9 Hz, J = 0.9 Hz, 1H, CH), 5.69 (dd, J = 17.6 Hz, J = 0.8 Hz, 1H, CH), 6.65 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H, CH), 7.18–7.20 (m, 2H, 2 × CH$_{Ar}$), 7.30–7.32 (m, 2H, 2 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 16.86 (CH$_3$), 113.22 (CH$_2$), 126.62 (4 × CH), 134.57 (C), 136.20 (CH), 137.99 (C).

2.3.6. 2-Vinylnaphthalene

Prepared from 2-naphthaldehyde and purified by flash chromatography, acetone: petroleum ether (1:9). White powder, 80%, mp = 60–63 °C. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 5.32 (dd, J = 10.8 Hz, J = 0.8 Hz, 1H, CH), 5.86 (dd, J = 17.6 Hz, J = 0.8 Hz, 1H, CH), 6.87 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H, CH), 7.41–7.46 (m, 2H, 2 × CH$_{Ar}$), 7.62 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, CH$_{Ar}$), 7.73 (s, 1H, CH$_{Ar}$), 7.78–7.80 (m, 3H, 3 × CH$_{Ar}$). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 114.21 (CH$_2$), 123.23 (CH), 125.95 (CH), 126.28 (CH), 126.42 (CH), 127.71 (CH), 128.10 (CH), 128.20 (CH), 133.21 (C), 133.61 (C), 135.07 (C), 136.99 (CH).

2.4. General procedure for stilbene aldehydes (**6**–**15**)

In a Schlenk flask, equipped with a reflux condenser and flushed with argon, montmorillonite-supported PdCl$_2$ catalyst [37] (0.01 g for every 5 mmol of 4-bromobenzaldehyde), 4-bromobenzaldehyde (1 equiv.), sodium acetate (2 equiv.) and DMF (2 mL for every 1 mmol of 4-bromobenzaldehyde) were stirred for 5 min under argon atmosphere. An appropriate styrene (1 equiv.) in DMF (1 mL for every 5 mmol) was added in one portion and mixture was refluxed until substrates disappeared on TLC (~3 h). The mixture was cooled to room temperature, poured into water and extracted with dichloromethane. Combined organic layers were washed with brine and dried with anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the crude product was vacuum dried.

2.4.1. (E)-4-Styrylbenzaldehyde (**6**)

Prepared from styrene (0.69 g, 6.5 mmol) and crystallized from toluene. 1.08 g (96%) of a white microcrystalline product, mp = 108–110 °C, lit. [38] mp = 107–109 °C. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 7.13 (d, J = 16.4 Hz, 1H, CH), 7.25 (d, J = 16.4 Hz, 1H, CH), 7.30–7.32 (m, 1H, CH$_{Ar}$), 7.35–7.39 (m, 2H, 2 × CH$_{Ar}$), 7.53 (d, J = 7.2 Hz, 2H, 2 × CH$_{Ar}$), 7.64 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.85 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 9.98 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 126.93 (3 × CH), 127.34 (CH), 128.51 (CH), 128.84 (2 × CH), 130.25 (2 × CH), 132.21 (2 × CH), 135.34 (C), 136.56 (C), 143.44 (C), 191.62 (CHO).

2.4.2. (E)-4-(4-Nitrostyryl)benzaldehyde (**7**)

Prepared from 1-nitro-4-vinylbenzene (0.500 g, 3.35 mmol), yielding 0.84 g (99%), of an orange crystalline product. Crystallized from toluene, mp = 195–197 °C, lit. [39] mp = 211–212 °C. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 7.28 (s, 1H, CH), 7.28 (s, 1H, CH), 7.66 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.69 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.90 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 8.24 (d, 2H, J = 8.4 Hz, 2 × CH$_{Ar}$), 10.01 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 124.23 (2 × CH), 127.33 (2 × CH), 127.47 (2 × CH), 129.56 (CH), 130.30 (2 × CH), 131.79 (CH), 136.16 (C), 142.05 (C), 142.94 (C), 147.32 (C), 191.47 ($\underline{C}$HO).

2.4.3. (E)-4-(4-Methylstyryl)benzaldehyde (**8**)

Prepared from 1-methyl-4-vinylbenzene (1.20 g, 10.2 mmol) and crystallized from toluene, yielding 2.05 g (90%) of pale yellow, crystalline product, mp = 189–193 °C, lit. [40] mp = 182.1–182.8 °C. ^{1}H NMR (CDCl$_3$, 700 MHz); δ ppm: 2.36 (s, 3H, CH$_3$), 7.08 (d, J = 16.1 Hz, 1H, CH), 7.18 (d, J = 7.0 Hz, 2H, 2 × CH$_{Ar}$), 7.22 (d, J = 16.8 Hz, 1H, CH), 7.43 (d, J = 7.0 Hz, 2H, 2 × CH$_{Ar}$), 7.62 (d, J = 7.0 Hz, 2H, 2 × CH$_{Ar}$), 7.84 (d, J = 7.7 Hz, 2H, 2 × CH$_{Ar}$), 9.97 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, 400 MHz); δ ppm: 21.36 (CH$_3$), 126.34 (CH), 126.79 (2 × CH), 126.87 (2 × CH), 129.59 (2 × CH), 130.26 (2 × CH), 132.19 (CH), 133.80 (C), 135.17 (C), 138.64 (C), 143.69 (C), 191.67 ($\underline{C}$HO).

2.4.4. (E)-4-(4-Methoxystyryl)benzaldehyde (**9**)

Prepared from 1-methoxy-4-vinylbenzene (1.61 g, 12.0 mmol) and crystallized from toluene, yielding 1.34 g (47%), of pale yellow crystalline product, mp = 148–150 °C, lit. [41] mp = 146–148 °C. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 3.83 (s, 3H, CH$_3$), 6.90 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 6.99 (d, J = 16.0 Hz, 1H, CH), 7.20 (d, J = 16.0 Hz, 1H, CH), 7.47 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.61 (d, J = 8.0 Hz, 2H, 2 × CH$_{Ar}$), 7.84 (d, J = 8.0 Hz, 2H, 2 × CH$_{Ar}$), 9.96 (s, 1H, C$\underline{H}$O). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 55.34 (CH$_3$), 114.30 (2 × $\underline{C}$H), 125.17 (CH), 126.60 (2 × CH), 128.26 (2 × CH), 129.34 (C), 130.26 (2 × CH), 131.79 (CH), 135.00 (C), 143.86 (C), 160.01 (C), 191.61 ($\underline{C}$HO).

2.4.5. (E)-4-(4-Fluorostyryl)benzaldehyde (**10**)

Prepared from 1-fluoro-4-vinylbenzene (1.46 g, 12.0 mmol), yielding 1.11 g (41%) of a creamy-white powder, mp = 120–122 °C, lit. [38] mp = 119.9–120.6 °C. ^{1}H NMR (CDCl$_3$, 400 MHz); δ ppm: 7.02–7.08 (m, 3H, 2 × CH$_{Ar}$, CH), 7.20 (d, J = 16.4 Hz, 1H, CH), 7.50 (dd, J = 8.4 Hz, J = 5.2 Hz, 2H, 2 × CH$_{Ar}$), 7.62 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 7.85 (d, J = 8.4 Hz, 2H, 2 × CH$_{Ar}$), 10.01 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, 100 MHz); δ ppm: 115.84 (CH), 116.07 (CH), 126.94 (CH), 127.14 (2 × CH), 128.56 (2 × CH), 130.32 (CH), 130.92 (C), 132.84 (2 × CH), 135.47 (C), 143.34 (C), 162.91 (C, d, J = 248.8 Hz), 191.65 ($\underline{C}$HO).

*2.4.6. (E)-4-(4-Chlorostyryl)benzaldehyde (**11**)*

Prepared from 1-chloro-4-vinylbenzene (1.41 g, 10.2 mmol), yielding 2.45 g (99%) of a pale yellow crystalline product. Crystallized from toluene, mp = 108–110 °C. ^{1}H NMR ($CDCl_3$, 700 MHz); δ ppm: 7.10 (d, J = 16.1 Hz, 1H, CH), 7.19 (d, J = 16.1 Hz, 1H, CH), 7.34 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 7.46 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 7.63 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 7.86 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 9.98 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 126.98 (2 × CH), 127.94 (CH), 128.06 (2 × CH), 129.06 (2 × CH), 130.29 (2 × CH), 130.82 (CH), 134.18 (C), 135.07 (C), 135.51 (C), 143.04 (C), 191.57 ($\underline{C}HO$). Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.52; H, 4.60.

*2.4.7. (E)-4-(4-(Trifluoromethyl)styryl)benzaldehyde (**12**)*

Prepared from 1-(trifluoromethyl)-4-vinylbenzene (1.72 g, 10.0 mmol), and crystallized from toluene, yielding 1.08 g (39%) of a yellow crystalline product, mp = 119–121 °C, lit. [42] mp = 128–130 °C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ ppm: 7.20 (d, J = 16.4 Hz, 1H, CH), 7.26 (d, J = 16.4 Hz, 1H, CH), 7.62 (s, 4H, 4 × CH_{Ar}), 7.66 (d, J = 8.4 Hz, 2H, 2 × CH_{Ar}), 7.88 (d, J = 8.4 Hz, 2H, 2 × CH_{Ar}), 10.0 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 125.79 (q, J = 3.8 Hz, 2 × CH), 126.99 (2 × CH), 127.21 (2 × CH), 129.83 (CH), 129.94 (C), 130.27 (2 × CH), 130.49 (CH), 135.82 (C), 139.99 (2 × C), 142.59 (C), 191.53 ($\underline{C}HO$).

*2.4.8. (E)-4-(4-(Methylthio)styryl)benzaldehyde (**13**)*

Prepared from methyl(4-vinylphenyl)sulfane (1.50 g, 10.0 mmol) and crystallized from toluene, yielding 1.22 g (48%), of a creamy-white crystalline product, mp = 148–150 °C. ^{1}H NMR ($CDCl_3$, 700 MHz); δ ppm: 2.50 (s, 3H, CH_3), 7.08 (d, J = 16.1 Hz, 1H, CH), 7.20 (d, J = 16.8 Hz, 1H, CH), 7.23 (d, J = 8.4 Hz, 2H, 2 × CH_{Ar}), 7.45 (d, J = 8.4 Hz, 2H, 2 × CH_{Ar}), 7.62 (d, J = 8.4 Hz, 2H, 2 × CH), 7.85 (d, J = 8.4 Hz, 2H, 2 × CH_{Ar}), 9.97 (s, 1H, CHO). ^{13}C NMR 15.94 (CH_3), 126.83 (2 × CH), 126.97 (CH), 127.06 (2 × CH), 127.71 (2 × CH), 130.26 (2 × CH), 131.79 (CH), 133.58 (C), 135.46 (C), 139.62 (C), 143.73 (C), 191.91 ($\underline{C}HO$).

*2.4.9. (E)-4-(3,4,5-Trimethoxystyryl)benzaldehyde (**14**)*

Prepared from 1,2,3-trimethoxy-5-vinylbenzene (1.94 g, 10.0 mmol) and crystallized from toluene, yielding 1.37 g (46%), of a creamy-yellow powder, mp = 158–160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ ppm: 3.86 (s, 3H, CH_3), 3.91 (s, 6H, 2 × CH_3), 6.75 (s, 2H, 2 × CH_{Ar}), 7.02 (d, J = 16.0 Hz, 1H, CH), 7.17 (d, J = 16.0 Hz, 1H, CH), 7.63 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 7.85 (d, J = 8.0 Hz, 2H, 2 × CH_{Ar}), 9.98 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 56.19 (2 × CH_3), 61.00 (CH_3), 104.10 (2 × CH), 126.77 (CH), 126.80 (2 × CH), 130.26 (2 × CH), 132.16 (CH), 132.24 (C), 135.30 (C), 138.76 (C), 143.34 (C), 153.51 (2 × C), 191.56 ($\underline{C}HO$). Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.58; H, 6.05.

*2.4.10. (E)-4-(2-(Naphthalen-2-yl)vinyl)benzaldehyde (**15**)*

Prepared from 2-vinylnaphthalene (1.54 g, 10.0 mmol) and crystallized from toluene, yielding 1.52 g (59%), of a creamy-white crystalline product, mp = 162–164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ ppm: 6.68 (d, J = 12.2 Hz, 1H, CH), 6.90 (d, J = 12.2 Hz, 1H, CH), 7.40–7.50 (m, 3H, CH_{Ar}, 2 × CH), 7.64–7.75 (m, 4H, 4 × CH_{Ar}), 7.80–7.89 (m, 4H, 4 × CH_{Ar}), 9.99 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 123.36 (CH), 126.43 (CH), 126.57 (CH), 126.93 (2 × CH), 127.62 (CH), 127.63 (CH), 127.77 (CH), 128.18 (CH), 128.56 (CH), 130.30 (2 × CH), 132.30 (CH), 133.42 (C), 133.61 (C), 134.04 (C), 135.36 (C), 143.47 (C), 191.62 ($\underline{C}HO$). Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.50; H, 5.50.

*2.5. General procedure for aryl–vinyl benzodifurans (**16**–**25**)*

Triphenylphosphonium salt (**5**) (1.18 g, 1 mmol) and lithium hydroxide monohydrate (0.11 g, 2.7 mmol) in 2-propanol (4 mL) were stirred for 10 min at rt. An appropriate aldehyde (2 mmol) was added and the mixture was refluxed for 3–5 h (TLC). After cooling the mixture was diluted with water (30 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (2 × 30 mL) and dried with anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the crude product was vacuum dried and purified using flash chromatography (dichloromethane). The obtained *E*/*Z* mixture of isomers was refluxed for 3 h in *p*-xylene (5 mL) with a small crystal of iodine. Cooled, filtered, washed with diethyl ether (2 × 5 mL), and dried under vacuum.

*2.5.1. Dioctyl 2,6-bis((E)-4-((E)-styryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**16**)*

Prepared from aldehyde **6**, 0.75 g (86%) of an orange solid, mp = 204–206 °C. ^{1}H NMR ($CDCl_3$, 700 MHz); δ ppm: 0.88 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.31–1.32 (m, 8H, 4 × CH_2), 1.35–1.38 (m, 4H, 2 × CH_2), 1.44 (m, 4H, 2 × CH_2), 1.56 (m, 4H, 2 × CH_2), 1.91 (m, 4H, 2 × CH_2), 4.44 (t, J = 7.0 Hz, 4H, 2 × CH_2), 7.10 (d, J = 16.2 Hz, 2H, 2 × CH), 7.15 (d, J = 16.2 Hz, 2H, 2 × CH), 7.25–7.27 (m, 2H, 2 × CH_{Ar}), 7.34–7.37 (m, 4H, 4 × CH_{Ar}), 7.51–7.53 (m, 8H, 8 × CH_{Ar}), 7.59–7.61 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.91 (d, J = 16.2 Hz, 2H, 2 × CH), 8.01 (s, 2H, 2 × CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 14.13 (2 × CH_3), 22.70 (2 × CH_2), 26.34 (2 × CH_2), 28.91 (2 × CH_2), 29.28 (2 × CH_2), 29.37 (2 × CH_2), 31.86 (2 × CH_2), 64.89 (2 × CH_2), 103.14 (2 × CH), 109.25 (2 × C), 115.33 (2 × CH), 125.64 (2 × C), 126.65 (4 × CH), 126.99 (4 × CH), 127.90 (2 × CH), 127.99 (4 × CH), 128.01 (2 × CH), 128.76 (4 × CH), 129.54 (2 × CH), 135.26 (2 × CH), 135.39 (2 × C), 135.45 (2 × C), 137.14 (2 × C), 138.35 (2 × C), 151.73 (2 × C), 160.94 (2 × C). IR (ATR)ν_{max} cm^{-1}: 3026, 2948, 2920, 2849, 1697, 1622, 1596, 1565, 1549, 1448, 1417, 1397, 1375, 1354, 1281, 1248, 1206, 1193, 1154, 1058, 961, 857, 812, 749, 720, 703, 688. Anal. Calcd. for $C_{60}H_{62}O_6$: C, 81.97; H, 7.11. Found: C, 82.50; H, 7.05.

*2.5.2. Dioctyl 2,6-bis((E)-4-((E)-4-nitrostyryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**17**)*

Prepared from aldehyde **7**, 0.89 g (92%) of a red solid, mp = 210–212 °C. ^{1}H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.32–1.38 (m, 8H, 4 × CH_2), 1.44–1.45 (m, 4H, 2 × CH_2), 1.52–1.57 (m, 4H, 2 × CH_2), 1.90–1.94 (m, 4H, 2 × CH_2), 4.45 (t, J = 7.0 Hz, 4H, 2 × CH_2), 7.15 (d, J = 16.3 Hz, 2H, 2 × CH), 7.23 (d, J = 16.3 Hz, 2H, 2 × CH), 7.54 (d, J = 8.0 Hz, 4H, 4 × CH_{Ar}), 7.57 (d, J = 16.2 Hz, 2H, 2 × CH), 7.61 (d, J = 14.0 Hz, 8H, 8 × CH_{Ar}), 7.92 (d, J = 16.2 Hz, 2H, 2 × CH), 8.01 (s, 2H, 2 × CH_{Ar}), 8.20 (d, J = 8.4 Hz, 4H, 4 × CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 14.14 (2 × CH_3), 22.70 (2 × CH_2), 26.34 (2 × CH_2), 28.91 (2 × CH_2), 29.28 (2 × CH_2), 29.36 (2 × CH_2), 31.86 (2 × CH_2), 64.95 (2 × CH_2), 103.24 (2 × CH), 109.61 (2 × C), 115.99 (2 × CH), 124.20 (4 × CH), 125.68 (2 × C), 126.92 (2 × CH), 126.95 (4 × CH), 127.50 (4 × CH), 128.04 (4 × CH), 132.49 (2 × CH), 134.82 (2 × CH), 136.55 (2 × C), 137.02 (2 × C), 143.59 (2 × C), 146.87 (2 × C), 151.77 (2 × C), 160.82 (2 × C), 164.13 (2 × C). IR (ATR)ν_{max} cm^{-1}: 2952, 2918, 2847, 1704, 1623, 1586, 1565, 1511, 1342, 1208, 1194, 1108, 1082, 1049, 964, 853, 839, 809, 748, 722, 703, 685. Anal. Calcd. for $C_{60}H_{60}N_2O_{10}$: C, 74.36; H, 6.24; N, 2.89. Found: C, 74.55; H, 6.40; N, 3.04.

*2.5.3. Dioctyl 2,6-bis((E)-4-((E)-4-methylstyryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**18**)*

Prepared from aldehyde **8**, 0.63 g (70%) of an orange solid, mp = 248–250 °C. ^{1}H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.23–1.37 (m, 8H, 4 × CH_2), 1.42–1.49 (m, 4H, 2 × CH_2), 1.52–1.56 (m, 4H, 2 × CH_2), 1.91 (t, J = 7.0 Hz, 4H, 2 × CH_2), 4.44 (t, J = 7.0 Hz, 4H, 2 × CH_2), 7.06 (d, J = 17.5 Hz, 2H, 2 × CH), 7.14 (d, J = 16.1 Hz, 2H, 2 × CH), 7.17 (d, J = 7.7 Hz, 4H,

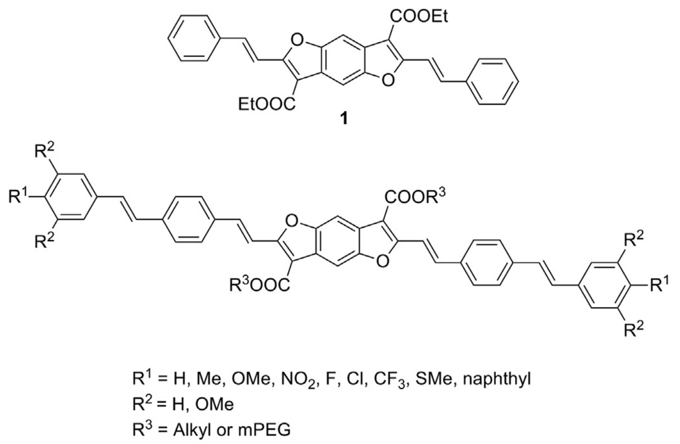


Fig. 1. Molecular structure of the prepared aryl–vinyl **BDF**s.

4 × CH_{Ar}), 7.42 (d, $J = 7.7$ Hz, 4H, 4 × CH_{Ar}), 7.52 (d, $J = 7.7$ Hz, 4H, 4 × CH_{Ar}), 7.60–7.64 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.93 (d, $J = 16.8$ Hz, 2H, 2 × CH), 8.03 (s, 2H, 2 × CH_{Ar}). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 3021, 2950, 2916, 2849, 1703, 1622, 1590, 1562, 1547, 1513, 1452, 1420, 1398, 1354, 1282, 1251, 1265, 1194, 1150, 1081, 1048, 963, 853, 818, 801, 781, 721, 704. Anal. Calcd. for $C_{62}H_{66}O_6$: C, 82.09; H, 7.33. Found: C, 82.52; H, 7.31.

2.5.4. *Dioctyl 2,6-bis((E)-4-((E)-4-methoxystyryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**19**)*

Prepared from aldehyde **9**, 0.62 g (66%) of an orange solid, mp = 218–220 °C. ^{1}H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, $J = 7.0$ Hz, 6H, 2 × CH_3), 1.30–1.32 (m, 8H, 4 × CH_2), 1.37 (m, 4H, 2 × CH_2), 1.44 (m, 4H, 2 × CH_2), 1.54–1.58 (m, 4H, 2 × CH_2), 1.91 (m, 4H, 2 × CH_2), 3.82 (s, 6H, 2 × CH_3), 4.44 (t, $J = 7.0$ Hz, 4H, 2 × CH_2), 6.89 (d, $J = 9.1$ Hz, 4H, 4 × CH_{Ar}), 6.96 (d, $J = 16.1$ Hz, 2H, 2 × CH), 7.11 (d, $J = 16.1$ Hz, 2H, 2 × CH), 7.59–7.62 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.90 (d, $J = 16.1$ Hz, 2H, 2 × CH), 8.01 (s, 2H, 2 × CH_{Ar}). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 2926, 2916, 2848, 1703, 1603, 1590, 1563, 1511, 1354, 1302, 1251, 1206, 1194, 1172, 1150, 1079, 1051, 1032, 967, 855, 826, 803, 782. Anal. Calcd. for $C_{62}H_{66}O_8$: C, 79.29; H, 7.08. Found: C, 78.82; H, 7.03.

2.5.5. *Dioctyl 2,6-bis((E)-4-((E)-4-fluorostyryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**20**)*

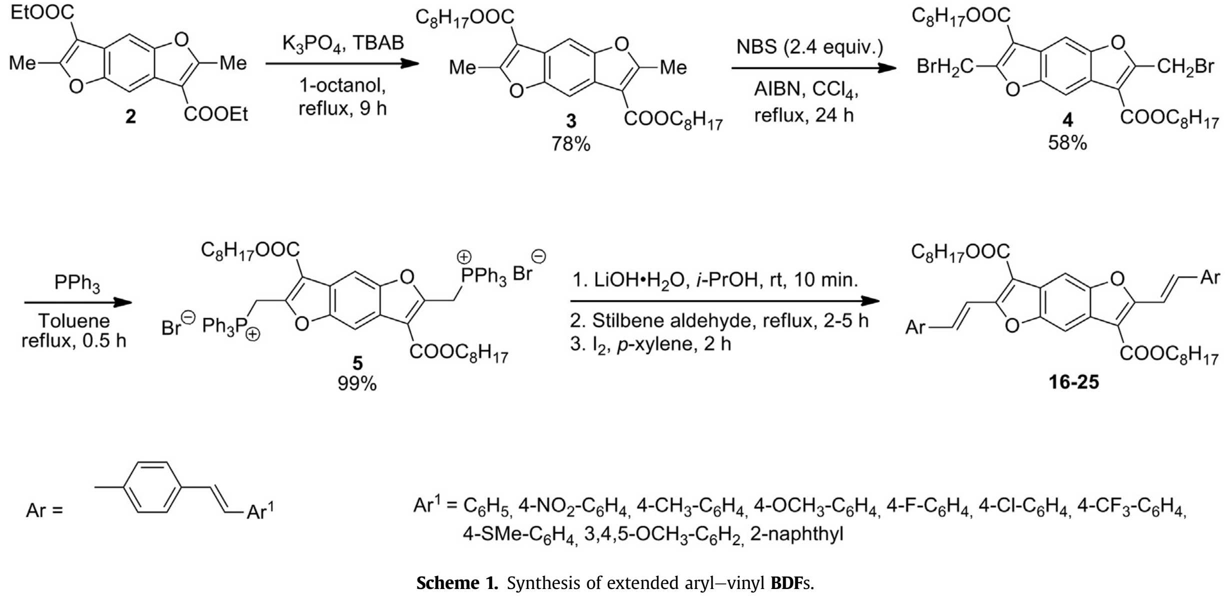
Prepared from aldehyde **10**, 0.58 g (63%) of an orange solid, mp = 235–237 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 0.88 (t, $J = 7.2$ Hz, 6H, 2 × CH_3), 1.31–1.42 (m, 16H, 8 × CH_2), 1.49–1.60 (m, 4H, 2 × CH_2), 1.85–1.95 (m, 4H, 2 × CH_2), 4.44 (t, $J = 7.2$ Hz, 4H, 2 × CH_2), 6.98–7.07 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.12 (d, $J = 16.0$ Hz, 2H, 2 × CH), 7.47–7.53 (m, 8H, 8 × CH_{Ar}), 7.61–7.65 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.94 (d, 2H, $J = 16.4$ Hz, 2 × CH), 8.02 (s, 2H, 2 × CH_{Ar}). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 2949, 2920, 2845, 1703, 1564, 1549, 1509, 1462, 1454, 1421, 1399, 1355, 1283, 1230, 1207, 1196, 1155, 1081, 1048, 966, 853, 825, 781, 721, 703. Anal. Calcd. for $C_{60}H_{60}F_2O_6$: C, 78.75; H, 6.61. Found: C, 78.51; H, 6.63.

2.5.6. *Dioctyl 2,6-bis((E)-4-((E)-4-chlorostyryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**21**)*

Prepared from aldehyde **11**, 0.49 g (52%) of an orange solid, mp = 248–250 °C. ^{1}H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, $J = 7.0$ Hz, 6H, 2 × CH_3), 1.23–1.39 (m, 8H, 4 × CH_2), 1.42–1.46 (m, 4H, 2 × CH_2), 1.54–1.58 (m, 4H, 2 × CH_2), 1.91 (t, $J = 7.0$ Hz, 4H, 2 × CH_2), 4.44 (t, $J = 7.0$ Hz, 4H, 2 × CH_2), 7.06 (d, $J = 16.8$ Hz, 2H, 2 × CH), 7.10 (d, $J = 16.8$ Hz, 2H, 2 × CH), 7.51–7.54 (m, 4H, 4 × CH_{Ar}), 7.60–7.66 (m, 6H, 4 × CH_{Ar}, 2 × CH), 7.93 (d, 2H, $J = 16.1$ Hz, 2 × CH), 8.02 (s, 2H, 2 × CH_{Ar}). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 2922, 2846, 1703, 1561, 1487, 1354, 1279, 1194, 1150, 1115, 1087, 1055, 1011, 962, 855, 824, 799, 782, 723, 703, 663. Anal. Calcd. for $C_{60}H_{60}Cl_2O_6$: C, 76.02; H, 6.38. Found: C, 76.34; H, 6.33.

2.5.7. *Dioctyl 2,6-bis((E)-4-((E)-4-(trifluoromethyl)styryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**22**)*

Prepared from aldehyde **12**, 0.53 g (52%) of an orange solid, mp = 242–244 °C. ^{1}H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, $J = 7.0$ Hz, 6H, 2 × CH_3), 1.30–1.34 (m, 8H, 4 × CH_2), 1.36–1.41 (m, 4H, 2 × CH_2), 1.44 (m, 4H, 2 × CH_2), 1.55–1.58 (m, 4H, 2 × CH_2), 1.91 (m, 4H, 2 × CH_2), 4.45 (t, $J = 7.0$ Hz, 4H, 2 × CH_2), 7.15 (d, $J = 16.1$ Hz, 2H, 2 × CH), 7.18 (d, $J = 16.1$ Hz, 2H, 2 × CH), 7.54 (d, $J = 7.7$ Hz, 4H, 4 × CH), 7.60–7.63 (m, 14H, 14 × CH_{Ar}), 7.93 (d, 4H, $J = 16.1$ Hz, 2 × CH), 8.02 (s, 2H, 2 × CH_{Ar}). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 2952, 2921, 2849, 1704, 1611, 1420, 1328, 1284, 1264, 1187, 1157, 1108, 1066, 1056, 1015, 1015, 961, 853, 830, 802,

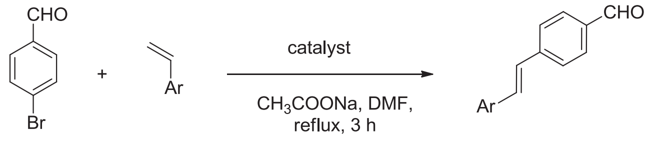


Scheme 1. Synthesis of extended aryl–vinyl **BDF**s.

Table 1
Solubility of 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate esters in common solvents.

R^3	Reaction yield [%]	Solubility at 20°C/at bp [μmol/mL]										
		H_2O	Et_2O	MeOH	EtOH	Acetone	Ethyl acetate	THF	CH_2Cl_2	$CHCl_3$	Toluene	PE
C_2H_5	–	<0.1/1.0	<0.1/1.8	<0.1/5.1	0.15/27	5.4/33	11/160	38/270	145/317	260/>1000	23/>1000	<0.1/1.5
C_5H_{11}	60	<0.1/<0.1	24/140	<0.1/31	0.12/>1000	16/650	25/>1000	217/>1000	620/>1000	>1000/>1000	120/>1000	1.0/13
C_8H_{17}	78	<0.1/<0.1	28/500	<0.1/20	0.1/>1000	9.0/>1000	27/>1000	270/>1000	680/>1000	>1000/>1000	158/>1000	3.2/210
$C_{10}H_{21}$	61	<0.1/<0.1	7.2/54	<0.1/1.8	<0.1/630	0.7/190	2.2/>1000	70/>1000	170/>1000	255/>1000	125/>1000	1.1/41
$C_{18}H_{37}$	76	<0.1/<0.1	<0.1/<0.1	<0.1/<0.1	<0.1/<0.1	<0.1/<0.1	<0.1/64	<0.1/450	0.5/23	6/384	0.5/>1000	<0.1/<0.1
mPEG 500	5	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞	<0.1/<0.1

Table 2
Synthesis of stilbene aldehydes using montmorillonite-supported palladium catalyst (12% wt.).



6-15

Ar	Product	Yield, %
C_6H_5	**6**	96
4-NO_2-C_6H_4	**7**	99
4-CH_3-C_6H_4	**8**	90
4-OCH_3-C_6H_4	**9**	47
4-F-C_6H_4	**10**	41
4-Cl-C_6H_4	**11**	99
4-CF_3-C_6H_4	**12**	39
4-SMe-C_6H_4	**13**	48
3,4,5-OCH_3-C_6H_2	**14**	46
2-Naphthyl	**15**	59

783, 703. Anal. Calcd. for $C_{62}H_{60}F_6O_6$: C, 73.36; H, 5.96. Found: C, 73.55; H, 5.99.

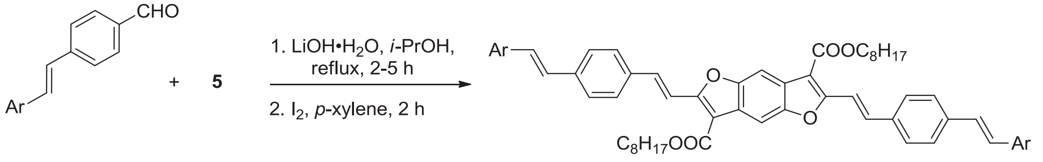
2.5.8. *Dioctyl 2,6-bis((E)-4-((E)-4-(methylthio)styryl)styryl)benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**23**)*

Prepared from aldehyde **13**, 0.47 g (48%) of an orange solid, mp = 210–212 °C. ^1H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.90 (t, $J = 7.0$ Hz, 6H, $2 \times CH_3$), 1.23–1.37 (m, 8H, $4 \times CH_2$), 1.44–1.56 (m, 8H, $4 \times CH_2$), 1.91 (t, $J = 7.0$ Hz, 4H, $2 \times CH_2$), 2.50 (s, 6H, $2 \times CH_3$), 4.44 (t, $J = 7.0$ Hz, 4H, $2 \times CH_2$), 7.05 (d, $J = 16.1$ Hz, 2H, $2 \times CH$), 7.10 (d, $J = 15.4$ Hz, 2H, $2 \times CH$), 7.22–7.24 (m, 2H, $2 \times CH_{Ar}$), 7.43 (d, $J = 8.4$ Hz, 4H, $4 \times CH_{Ar}$), 7.50 (d, $J = 8.4$ Hz, 6H, $6 \times CH_{Ar}$), 7.59–7.61 (m, 6H, $4 \times CH_{Ar}$, $2 \times CH$), 7.91 (d, $J = 16.1$ Hz, 2H, $2 \times CH$), 8.01 (s, 2H, $2 \times CH_{Ar}$). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 2951, 2918, 2850, 1701, 1420, 1354, 1206, 1192, 1085, 1051, 961, 856, 819, 798, 782, 702. Anal. Calcd. for $C_{62}H_{66}O_6S_2$: C, 76.67; H, 6.85. Found: C, 76.88; H, 6.89.

2.5.9. *Dioctyl 2,6-bis((E)-4-((E)-3,4,5-trimethoxystyryl)styryl) benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**24**)*

Prepared from aldehyde **14**, 0.61 g (58%) of an orange solid, mp = 182–184 °C. ^1H NMR ($CDCl_3$, 700 MHz), δ ppm: 0.88 (t, $J = 7.0$ Hz, 6H, $2 \times CH_3$), 1.29–1.32 (m, 8H, $4 \times CH_2$), 1.36–1.39 (m, 4H, $2 \times CH_2$), 1.41–1.46 (m, 4H, $2 \times CH_2$), 1.91 (m, 4H, $2 \times CH_2$), 3.87 (s, 6H, $2 \times CH_3$), 3.92 (s, 12H, $4 \times CH_3$), 4.44 (t, $J = 7.0$ Hz, 4H, $2 \times CH_2$), 6.75 (s, 4H, $4 \times CH_{Ar}$), 7.01 (d, $J = 16.1$ Hz, 2H, $2 \times CH$), 7.09 (d, $J = 16.1$ Hz, 2H, $2 \times CH$), 7.52–7.54 (m, 4H, $2 \times CH$), 7.62–7.64 (m, 6H, $4 \times CH_{Ar}$, $2 \times CH$), 7.94 (d, $J = 16.1$ Hz, 2H, $2 \times CH$), 8.04 (s, 2H, $2 \times CH_{Ar}$). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 15.03 ($2 \times CH_3$), 23.64 ($2 \times CH_2$), 27.31 ($2 \times CH_2$), 29.93 ($2 \times CH_2$), 30.23 ($2 \times CH_2$), 30.33 ($2 \times CH_2$), 32.82 ($2 \times CH_2$), 57.22 ($4 \times CH_3$), 61.92 ($2 \times CH_3$), 65.83 ($2 \times CH_2$), 104.12 ($2 \times CH$), 105.09 ($4 \times CH$), 110.29 ($2 \times C$), 116.36 ($2 \times CH$), 126.66 ($2 \times C$), 127.86 ($4 \times CH$), 128.50 ($2 \times CH$), 128.95 ($4 \times CH$), 130.53 ($2 \times CH$), 133.86 ($2 \times C$), 136.16 ($2 \times CH$), 136.42 ($2 \times C$), 139.27 ($2 \times C$), 139.56 ($2 \times C$), 152.76 ($2 \times C$), 154.52 ($4 \times C$), 161.89 ($2 \times C$), 165.11 ($2 \times C$). IR (ATR)ν_{max} cm^{-1}: 2926, 2853, 1697, 1580, 1564, 1508, 1463, 1455, 1420, 1397, 1377, 1347, 1321, 1282, 1246, 1219, 1189, 1135, 1047, 999,

Table 3
The Wittig reaction of **BDF** salt **5** with stilbene aldehydes.



6-15 16-25

Stilbene aldehyde	Ar	Product	Yield, %
6	C_6H_5	**16**	86
7	4-NO_2-C_6H_4	**17**	92
8	4-CH_3-C_6H_4	**18**	70
9	4-OCH_3-C_6H_4	**19**	66
10	4-F-C_6H_4	**20**	63
11	4-Cl-C_6H_4	**21**	52
12	4-CF_3-C_6H_4	**22**	52
13	4-SMe-C_6H_4	**23**	48
14	3,4,5-OCH_3-C_6H_2	**24**	58
15	2-Naphthyl	**25**	73

Table 4
Physical properties of **BDF**s **16**–**25**.

Compound	Dichloromethane solution								Solid state
	λ_{abs} (nm)	ε M^{-1} cm^{-1}	λ_{em} (nm)	θ_F[a]	τ_F[b] (ns)	HOMO[c] (eV)	LUMO[c] (eV)	E_g (eV)	λ_{em}(nm)
16	445	119,600	495	0.62	1.40	−4.986	−2.345	2.641	560
17	455	123,200	495	<0.01	0.64	−5.347	−2.880	2.468	589
18	447	110,000	498	0.61	1.10	−4.929	−2.299	2.630	570
19	450	113,200	503	0.58	1.15	−4.836	−2.236	2.600	570
20	445	101,200	494	0.64	1.23	−5.024	−2.386	2.638	560
21	446	94,400	495	0.66	1.30	−5.094	−2.464	2.630	570
22	446	118,800	494	0.69	1.31	−5.184	−2.559	2.625	560
23	452	106,400	504	0.61	1.12	−4.895	−2.312	2.583	570 599
24	451	98,800	500	0.61	1.17	−4.920	−2.309	2.611	570
25	452	128,000	501	0.61	1.17	−4.966	−2.358	2.607	570
1	432	37,100	478	1.00	1.4	−5.584	−2.603	2.981	566

[a] Quantum yield measured with a JASCO FP-8500 spectrometer against fluorescein in 0.1 M NaOH as reference at $\lambda_{ex} = 460$ nm. A reference value of 0.9 for the fluorescein quantum yield was used for the calculation of θ_F. Absorbance of the dye solution between 0.041 and 0.099 at $\lambda_{abs} = 460$ nm.

[b] Fluorescence lifetime determined by time-correlated single-photon counting (TCSPC) with a PicoQuant (Germany) pulsed LED at $\lambda_{ex} = 376$ nm as light source. The same solution as that described above was used.

[c] Calculated using the B3LYP/6-31G(d,p).

969, 952, 848, 820, 797, 620. Anal. Calcd. for $C_{66}H_{74}O_{12}$: C, 74.83; H, 7.04. Found: C, 75.10; H, 7.16.

2.5.10. *Dioctyl 2,6-bis((E)-4-((E)-2-(naphthalen-2-yl)vinyl)styryl) benzo[1,2-b:4,5-b′]difuran-3,7-dicarboxylate (**25**)*

Prepared from aldehyde **15**, 0.71 g (73%) of an orange solid, mp = 234–236 °C. ^{1}H NMR (CDCl$_3$, 400 MHz), δ ppm: 0.81–0.89 (m, 6H, 2 × CH$_3$), 1.20–1.26 (m, 8H, 4 × CH$_2$), 1.32–1.58 (m, 8H, 4 × CH$_2$), 1.73–1.90 (m, 8H, 4 × CH$_2$), 4.33–4.44 (m, 4H, 2 × CH$_2$), 7.29–7.68 (m, 32H, 24 × CH$_{Ar,}$ 8 × CH). Solubility too low for ^{13}C NMR. IR (ATR)ν_{max} cm^{-1}: 3053, 3024, 2951, 2926, 2915, 2864, 2856, 1704, 1623, 1565, 1548, 1500, 1453, 1417, 1399, 1356, 1287, 1249, 1208, 1197, 1152, 1059, 961, 854, 818, 782, 746, 722, 703. Anal. Calcd. for $C_{68}H_{66}O_6$: C, 83.40; H, 6.79. Found: C, 83.85; H, 6.83.

3. Results and discussion

The aim of this work was the development and fluorescence characterization of new conjugated **BDF** aryl–vinyl systems containing four double bonds and at least four phenyl rings **16**–**25**, and their comparison with previously obtained aryl–vinyl **BDF**s, containing only two double bonds and two phenyl rings **1** (Fig. 1).

It was obvious that the emission wavelength of such extended systems would be shifted toward higher values in comparison to **1**, and it was interesting to know how the elongation of the conjugated system affects the fluorescence intensity. Separation of the substituted phenyl ring and **BDF** core with 1,4-divinylphenylene moiety would show more clearly the influence of aryl–vinyl substituents on the fluorescence of compounds represented by general formula, Fig. 1.

Their synthesis started from diethyl 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate (**2**), Scheme 1, which was prepared in 21% yield from easily available *p*-benzoquinone and ethyl acetoacetate using earlier described method [42]. Ethyl groups of **2** were replaced by alkyl or methoxypoly(ethylene glycol) groups via the transesterification reaction to improve the desired conjugated system solubility in common organic solvents. The process was carried out according to the Cepanec [43] method, using anhydrous potassium phosphate and *tert*-butylammonium bromide, as a phase transfer catalyst, in alcohol or toluene (Table 1).

The transesterification with alcohols proceeded in good yields whereas the mPEG 5000 ester could not been obtained using this procedure, and the mPEG 500 ester was obtained only in 5% yield. The best transesterification yield and good product solubility were achieved with 1-octanol and this derivative has been chosen for further transformations. Bromination of dioctyl 2,6-dimethylbenzo[1,2-*b*:4,5-*b*′]difuran-3,7-dicarboxylate (**3**) with NBS (2.4 equiv.) in the presence of catalytic amounts of AIBN, gave the 2,6-dibromo derivative (**4**) in 58% yield. The reaction of **4** with triphenylphosphine in boiling toluene produced the corresponding salt **5** in quantitative yield (Scheme 1).

Stilbene aldehydes **6**–**15** for the Wittig reaction were obtained from 4-bromobenzaldehyde and appropriate styrenes via the Heck coupling reaction. Commercially unavailable or expensive styrenes (4-nitrostyrene, 4-trifluoromethylstyrene, 1-(methylthio)-4-vinylbenzene, 3,4,5-trimethoxystyrene, and 2-vinylnaphthalene) were obtained via the Wittig reaction of an appropriate aldehyde and methyltriphenylphosphonium iodide.

The Heck coupling reaction of 4-bromobenzaldehyde and styrene, catalyzed by palladium acetate according to the Yao [44] method, gave in our hands the desired product only in 65% yield.

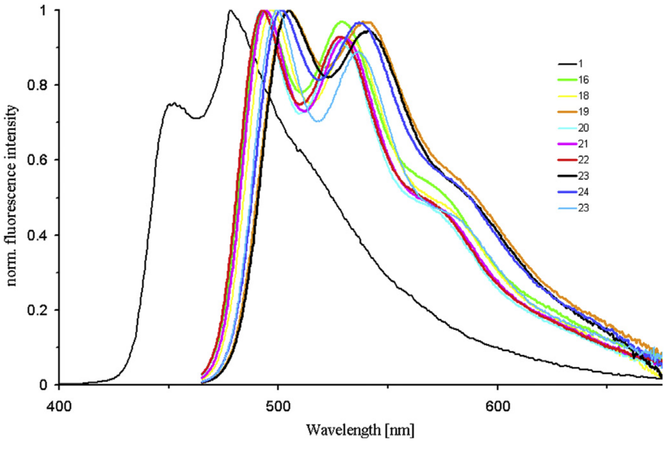


Fig. 2. Emission spectra of **16**–**25** in dichloromethane. Excitation wavelength $\lambda_{ex} = 460$ nm. Concentration set to an absorbance value between 0.04 and 0.10 to avoid the inner filter effect. The spectra are normalized to the maximal intensity. For comparison, the spectrum of **1** is also depicted ($\lambda_{ex} = 366$ nm).

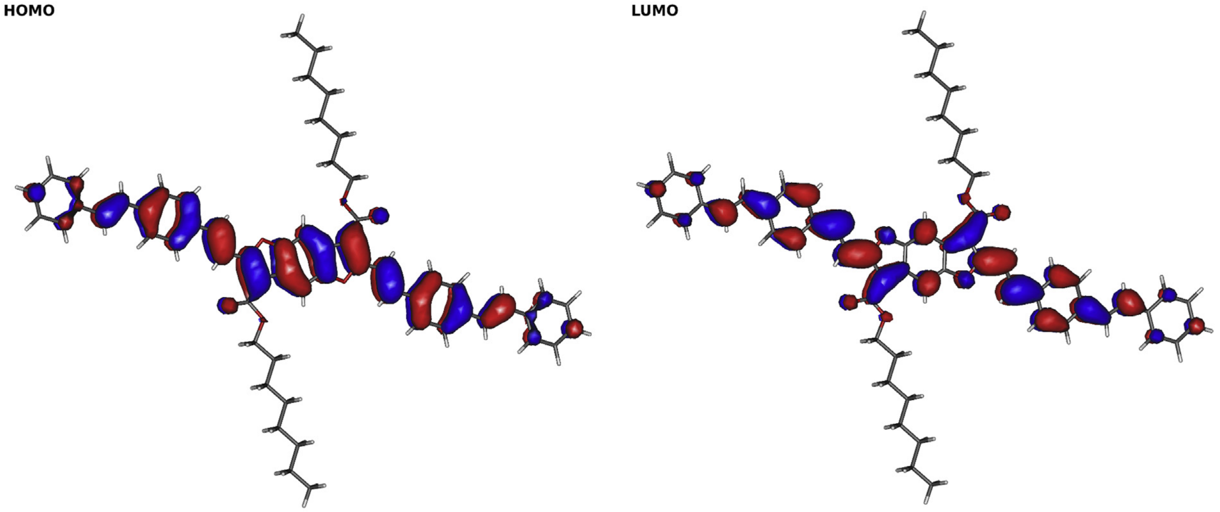


Fig. 3. HOMO and LUMO orbitals of **16** calculated within the B3LYP/6-31G(d,p) approach.

Better yields (96%), were obtained using the montmorillonite-supported palladium catalyst [45], and this catalytic system has been used for further research. The desired stilbene aldehydes were obtained in moderate to excellent yields (Table 2).

The Wittig reaction of stilbene aldehydes with **BDF** salt **5**, using lithium hydroxide monohydrate in isopropanol [45], monitored by TLC, was continued until the starting aldehyde faded (2–5 h). The products are shown in Table 3.

The products **16**–**25** were mixtures of *E*/*Z* isomers. The *E*/*Z* ratio assignment is based on the ^{1}H NMR coupling constants between hydrogen atoms at the double bonds. Pure *E* isomers were obtained by heating the mixture with a small amount of iodine in *p*-xylene for 2 h. The products were obtained in moderate to good yields, as amorphous orange to red solids. Unfortunately in some cases solubility was too low for recording ^{13}C NMR spectra.

Among the products **16**–**25**, the compound **25**, containing the 2-naphthyl group, exhibited the highest fluorescence intensity in dichloromethane solution, taken as a combination of the molar extinction coefficient and fluorescence quantum yield (Table 4). The fluorescence of other compounds is similar except 4-nitrophenyl derivative which exhibits no fluorescence. The nitroaromatics are effective fluorescence quenchers of most fluorophores [46]. This phenomenon is attributed to the photo-induced electron transfer (PET) process.

In the solid state, compound **20** (4-fluorophenyl), was the most fluorescent. The fluorescence of compounds **22** (4-trifluoromethylphenyl), **25** (2-naphthyl), **18** (4-methylphenyl), **16** (phenyl), was lower. Weaker fluorescence was observed for compounds **19** (4-methoxyphenyl), **21** (4-chlorophenyl), **23** (4-methylthiophenyl), and **24** (3,4,5-trimethoxyphenyl), whereas compound **17** (4-nitrophenyl) revealed no fluorescence. The emission spectra of **16**–**25** are shown in Fig. 2.

The results were compared to the previously obtained diethyl 2,6-di((*E*)-styryl)benzo[1,2-*b*:4,5-*b*′]difuran-3,7-dicarboxylate (**1**). It was found that elongation of the aryl–vinyl substituents of benzodifuran has no appreciable effect on the fluorescence intensity. Although the fluorescence quantum yield decreased in comparison to the mono aryl–vinyl system, the molar absorptivity increased significantly and resulted in equalization of the fluorescence intensity. The emission profiles and fluorescence maxima for all new aryl–vinyl benzodifuran derivatives are almost identical. This may suggest that the further separation of the substituted aryl end group from the benzodifuran core, the smaller is its impact on the wavelength of light emitted by the system. This leads to the conclusion that modification of the fluorophore structure should be made close to the benzodifuran core to affect the color of the emitted light.

An insight into the electronic structure of the investigated molecules was gained by the QM calculations within the B3LYP/6-31G(d,p). The calculations were performed with Gaussian 09 program package [47].

Fig. 3 presents the HOMO and LUMO orbitals of **16** which is representative of the 2,6-substituted benzodifurans. Visualization of the HOMO and LUMO molecular orbitals does not suggest any significant charge transfer during an electron excitation. The non-planar structure of desired compounds can effectively hinder intermolecular aggregation preventing strict packing of molecules and improving luminescence.

4. Conclusion

In summary, ten new aryl–vinyl **BDF**s containing four double bonds and at least four aromatic rings were obtained by a four step synthesis, involving the Heck and the Wittig reactions, with good overall yields. All of the new **BDF**s, except 4-nitrophenyl derivative, exhibit high fluorescence and quantum yields. Their comparison with previously obtained aryl–vinyl **BDF**s, containing only two double bonds and two phenyl rings, revealed similar fluorescence intensity despite a slightly lower quantum yields, due to higher molar extinction coefficient. The emission spectra of the new **BDF**s exhibit almost identical profiles and emission maxima, which are shifted to longer wavelengths in comparison to less conjugated aryl–vinyl **BDF**s.

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