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Synthesis of a new class of highly fluorescent aryl-vinyl benzo[1,2-*b*:4,5-*b*′]difuran derivatives

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ABSTRACT

The synthesis of 2-(2-arylvinyl)- and 2,6-di(2-arylvinyl)dibenzo[1,2-*b*:4,5-*b*′]furan derivatives for application in optoelectronics is described. Wittig reaction of the triphenylphosphonium bromides derived from diethyl 2,6-dimethylbenzofuro[5,6-b]furan-3,7-dicarboxylate with aryl aldehydes gave the products in 70–99% yield. The corresponding products derived from furfural and cinnamic aldehyde were also obtained. The prepared products reveal UV–Vis fluorescence with quantum yields, varying from 1% to 100%, and may be used as organic small molecule materials for organic light-emitting devices (OLED).

Conjugated π-electronic systems are important building blocks for dye-sensitized solar cells (DSSC)[1] and organic light-emitting devices (OLED).[2] Light-emitting polymers and organic small molecule materials are used for the production of OLEDs.[3] Among the latter, the most efficient fluorescent emitters yet reported belong to the distyrylarylenes[4] and oligo-phenyl vinyl compounds.[5] Despite numerous literature examples of the aforementioned conjugated π-electronic systems, little attention has been paid to heterocyclic compounds containing oxygen atoms. Benzodifuran derivatives, due to their fluorescent properties, represent an important group of compounds for OLED manufacturing. Recently, the first examples of benzodifuran small molecule materials,[6–10] and polymers,[11,12] were reported. Herein, the synthesis and fluorescence characterization of a novel group of substituted aryl-vinyl, heteroaryl-vinyl, and 4-phenyl-1,3-butadienyl benzodifurans designed for optoelectronic applications are described.

Diethyl 2,6-dimethylbenzofuro[5,6-*b*]furan-3,7-dicarboxylate (**1**) was easily prepared, in 25% yield, from *p*-benzoquinone and ethyl acetoacetate using the Griniev method.[13] Bromination of **1** with NBS (0.95 or 2.2 equiv) in the presence of a catalytic amount of AIBN, gave monobromo and 2,6-(dibromomethyl) derivatives **2** and **3** in 63% and 67% yields, respectively. The reactions of **2** and **3** with triphenylphosphine in boiling toluene produced the corresponding salts **4** and **5** (Scheme 1) in quantitative yields.

Ylides were generated from **4** and **5** for the Wittig reaction with aromatic aldehydes. The best yields of products were obtained using lithium hydroxide monohydrate in isopropanol as the solvent, according to the method of Antonioletti[14] (Tables 1 and 2). Reactions, monitored by TLC, were continued until the starting aldehyde was no longer apparent (0.5–2.5 h).

Pure *E* isomers of the products were obtained by heating *E/Z* mixtures with a small amount of iodine in *p*-xylene for 2 h. According to this procedure, the products were obtained in good yields as amorphous yellow to orange solids. The *E/Z* ratio assignment is based on the ^{1}H NMR coupling constants between hydrogen atoms at the double bond.

Furyl derivatives **13** and **23** decomposed under reflux in the I_2/*p*-xylene system, and crude *E/Z* mixtures were taken to fluorescence recording. All the products, except **13** and **23**, were stable in air and on exposure to direct sunlight.

Among products **6**–**15**, compound **11**, containing a *p*-chlorophenyl group (Table 3), exhibited the highest fluorescence intensity in dichloromethane, taken as a combination of the molar extinction coefficient and fluorescence quantum yield. The fluorescence for compounds **6** (phenyl), **7** (*p*-nitrophenyl), **10** (*p*-fluorophenyl), and **12** (*p*-bromophenyl) was lower, whereas compounds **8** and **9**, containing electron-donating groups, showed poor fluorescence in dichloromethane. In the solid state, **6** and **11** proved to be the most fluorescent, and unexpectedly for **9** (*p*-methoxyphenyl), high fluorescence was also observed.

In the case of 2,6-disubstituted benzodifurans **16**–**25**, similar trends were observed in dichloromethane solutions. Compounds

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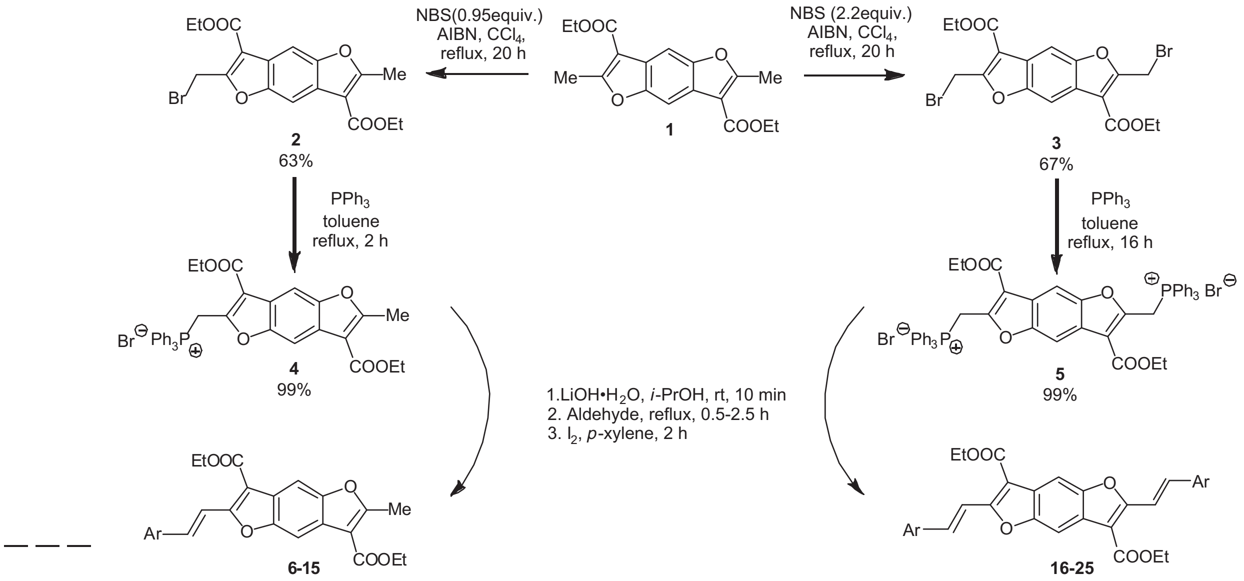

Scheme 1. Synthesis of aryl-vinyl benzodifuran derivatives.

Table 1
Synthesis of monosubstituted aryl-vinyl benzodifurans by reaction of **4** with various aldehydes

Aldehyde	Product	Yield (%)
Benzaldehyde	**6**	99
p-$O_2NC_6H_4CHO$	**7**	95
p-$CH_3C_6H_4CHO$	**8**	73
p-$CH_3OC_6H_4CHO$	**9**	73
p-FC_6H_4CHO	**10**	82
p-ClC_6H_4CHO	**11**	70
p-BrC_6H_4CHO	**12**	77
Furfural	**13**	94
9-Anthracenecarboxaldehyde	**14**	94
$C_6H_5CH{=}CHCHO$	**15**	79

Table 2
Synthesis of disubstituted aryl-vinyl benzodifurans by reaction of **5** with various aldehydes

Aldehyde	Product	Yield (%)
Benzaldehyde	**16**	89
p-$O_2NC_6H_4CHO$	**17**	99
p-$CH_3C_6H_4CHO$	**18**	76
p-$CH_3OC_6H_4CHO$	**19**	89
p-FC_6H_4CHO	**20**	77
p-ClC_6H_4CHO	**21**	88
p-BrC_6H_4CHO	**22**	96
Furfural	**23**	51
9-Anthracenecarboxaldehyde	**24**	82
$C_6H_5CH{=}CHCHO$	**25**	77

Table 3
Physical properties of benzodifurans **6**–**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)	Fluorescence intensity
6	368	42480	451	0.34	1.0	−5.743	−2.412	3.331	494	9217
7	411	32360	553	1.00	2.6	−5.944	−3.134	2.811	590	683
8	367	27940	456	0.07	0.2	−5.674	−2.360	3.315	520	4201
9	371	29240	471	0.01	0.1	−5.543	−2.284	3.259	519	7793
10	384	8080	486	0.27	1.5	−5.741	−2.414	3.327	550	1367
11	371	>120000	455	0.45	1.2	−5.783	−2.501	3.282	509	8440
12	370	32840	458	0.58	1.3	−5.780	−2.506	3.274	524	2313
13	384	4620	496	0.05	1.0	−5.591	−2.394	3.198	–	–
14	450	56220	558	0.04	0.7	−5.451	−2.553	2.898	570	282
15	407	33480	484	0.06	0.2	−5.576	−2.554	3.021	530	1641
16	432	37100	478	1.00	1.4	−5.584	−2.603	2.981	566	1855
17	422	42120	560	0.76	1.8	−5.888	−3.293	2.595	601	386
18	415	40020	483	0.66	1.2	−5.497	−2.542	2.955	567	9596
19	425	42600	498	0.18	0.1	−5.347	−2.453	2.894	570	549
20	431	37080	480	0.98	1.5	−5.585	−2.610	2.975	560	2408
21	418	39840	484	1.00	1.4	−5.647	−2.706	2.940	560	428
22	417	37640	484	1.00	1.5	−5.645	−2.712	2.933	568	924
23	428	40060	500	0.25	1.0	−5.406	−2.583	2.823	602	153
24	443	27220	557	0.01	1.6	−5.357	−2.707	2.651	565	26
25	456	44200	517	0.06	0.2	−5.393	−2.732	2.661	560	653

[a] Quantum yield measured against 9,10-diphenylanthracene in cyclohexane at λ_{ex} = 366 nm. Absorbance of the dye solution between 0.066 and 0.145 at λ_{abs} = 366 nm.

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

[c] Calculated using the B3LYP/6-311G(d,p) approach including the solvent (dichloromethane) effects via the PCM model.

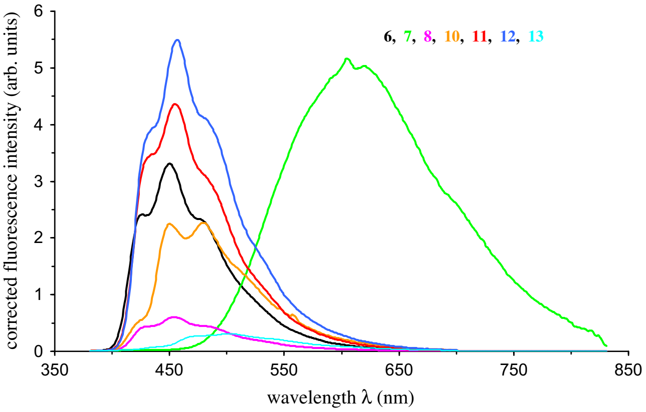

Figure 1. Emission spectra of selected 2-substituted benzodifurans in dichloromethane. Excitation wavelength, λ_{ex} = 366 nm. Concentration set to an absorbance value between 0.09 and 0.11 to avoid the inner filter effect. The spectra are corrected for the different absorbances to allow a quantitative comparison.

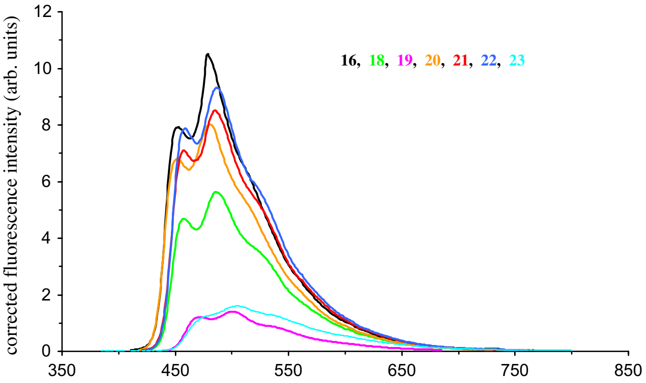

Figure 2. Emission spectra of selected 2,6-disubstituted benzodifurans in dichloromethane. Excitation wavelength, λ_{ex} = 366 nm. Concentration set to an absorbance value between 0.09 and 0.11 to avoid the inner filter effect. The spectra are corrected for the different absorbances to allow a quantitative comparison.

16 (phenyl), **17** (*p*-nitrophenyl), **18** (*p*-methylphenyl), **20** (*p*-fluorophenyl), **21** (*p*-chlorophenyl), and **22** (*p*-bromophenyl) exhibited the highest fluorescence intensities. Both 2-substituted and 2,6-disubstituted benzodifurans containing furyl (**13** and **23**), 9-anthryl (**14** and **24**), and cinnamic (**15** and **25**) moieties revealed very poor fluorescence.

The weak fluorescence observed for compounds **13** and **23** may be due to the fact that crude *E*/*Z* mixtures of isomers were used for the measurements, instead of the pure *E* isomer, as was the case for other compounds. This was due to the instability of these two compounds and may also explain the phenomenon of the long fluorescence lifetime observed for **13** despite the low fluorescence quantum yield. Unexpectedly, a similar long fluorescence lifetime was also observed for weakly fluorescent **24**, containing two anthracene moieties. The most intense emission spectra for the 2-substituted and 2,6-disubstituted benzodifurans are shown in Figures. 1 and 2.

Generally, 2,6-disubstituted benzodifurans revealed higher fluorescence, only for *p*-nitrophenyl, 9-anthryl, and *p*-cinnamic derivatives was the trend opposite. Also, the absorption and emission wavelength maxima for all disubstituted benzodifurans, except the 9-anthryl derivative, were shifted toward longer values. Although the emission spectra of 2,6-disubstituted benzodifurans (Fig. 2), revealed almost identical profiles and differed only in the intensity, the spectra of 2-substituted benzodifurans revealed different profiles and wavelength maxima (Fig. 1).

An insight into the electronic structure of the investigated molecules was gained from quantum mechanical calculations within the B3LYP/6-311G(d,p) approach including solvent (dichloromethane) effects via the PCM model. The calculations were performed with the Gaussian09[15] program package. Fig. 3 presents frontier orbitals for compounds **6** and **16** as representatives of 2-disubstituted and 2,6-substituted benzodifurans, respectively. In the case of the 2-substituted system, a significant charge transfer from the central ring of the benzodifuran moiety to the substituent is expected upon excitation. On the other hand, 2,6-disubstituted benzodifurans possess zero dipole moment due to symmetry in the ground state.

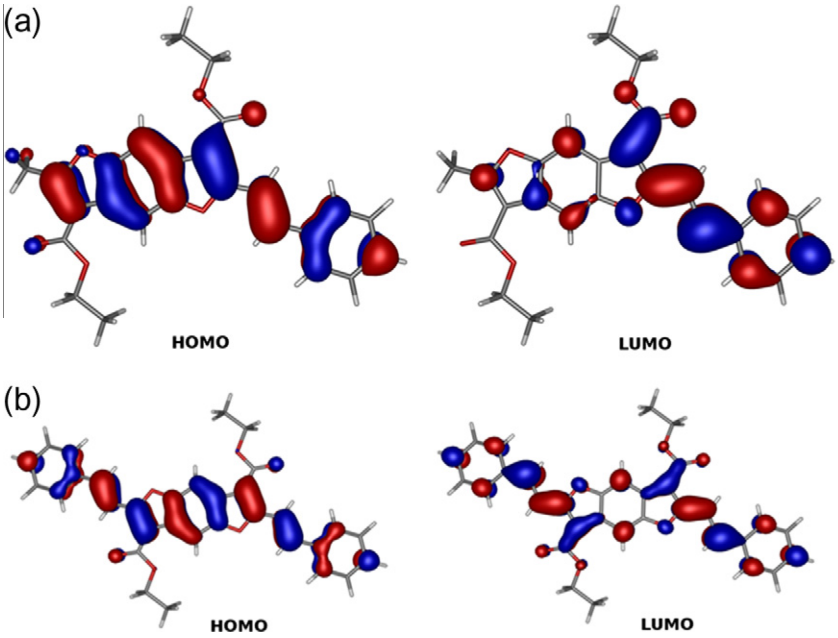

Figure 3. Frontier orbitals for (a) **6** and (b) **16** calculated within the B3LYP/6-311G(d,p) approach including the solvent (dichloromethane) effects via the PCM model.

In conclusion, twenty new 2-substituted and 2,6-disubstituted aryl-vinyl benzodifurans were synthesized in three steps and in good to excellent yields. Compounds **6**, **7**, **10**, **11**, **12**, **16**, **17**, **18**, **20**, **21**, and **22** exhibit high fluorescence activity with excellent quantum yields for **7**, **16**, **20**, **21**, and **22**, which might show potential as organic light-emitting devices. Further work on aryl-vinyl benzodifuran-based OLED devices is in progress.

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Supplementary data

Supplementary data (complete experimental procedures, spectral data characterization for compounds and HOMO/LUMO orbital visualization) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.05.087.

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