1-1-2008

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Abstract

Electroactive tetraarylbenzo[1,2-b:4,5-b′]difuran (BDF) and model diarylbenzofuran derivatives are synthesized and their structures are established by X-ray crystallography. Isolation and X-ray crystallographic characterization of the robust cation-radical salts of BDF derivatives confirm that a single charge in the BDFs is stabilized largely by the benzodifuran and coplanar α-aryl groups lying on the longitudinal axis. These findings suggest that the linear arrays of BDFs may allow the construction of molecular wires suitable for long-range electron transport.

The design and syntheses of new electroactive chromophores have attracted considerable attention over the past decade owing to their potential for the practical applications in the emerging areas of molecular electronics and nanotechnology. Tetraarylbenzo[1,2-b:4,5-b′]difurans (simply referred to hereafter as BDF), a largely unexplored class of electroactive chromophores, possess close structural similarities to the electroactive moieties utilized for the construction of, extensively explored, polyphenylenevinylene (PPV) and its alkoxy-substituted derivatives (i.e., Figure 1).

Although BDF derivatives have been known for over a century and can be easily prepared in excellent yields via Lewis acid-catalyzed condensations of benzoin or substituted benzoins with p-hydroquinone, their potential as electroactive materials has received little attention.
Our continuing interest in the design and syntheses of chromophores that form stable organic cation radicals led us to explore the potential of BDF derivatives as hole carriers. As such, the cation radicals, or hole carriers, are of fundamental importance to organic material science since they constitute the smallest unit that stabilizes a cationic charge as well as an unpaired electron.\(^{(5)}\)

Accordingly, in this report we describe the preparation of various tetraarylbenzodifurans (BDFs) as well as diarylbenzofurans (as model compounds), and show that BDFs are highly luminescent materials that undergo reversible electrochemical oxidations and form stable cation-radical salts that can be isolated in crystalline form. The structures of various neutral BDFs and their cation radicals are determined by X-ray crystallography and further corroborated by DFT calculations. The structural studies of BDF cation radicals allow us to delineate that a single charge in BDFs is stabilized largely by benzodifuran and the α-aryl groups lying on the longitudinal axis (shown in red in Figure 1) while the β-aryl groups on the vertical axis (shown in black in Figure 1) contribute little to the stabilization of the cationic charge. The details of these findings are described herein.

Thus, tetraphenylbenzodifuran (BDF1) was obtained by simply heating an intimate mixture of benzoin, \(p\)-hydroquinone, and zinc chloride in 2:1:2.5 molar ratio for 5–15 min. The resulting mixture was cooled to 22 °C and was triturated with dichloromethane and water. The dichloromethane layer was separated and washed with a 10% aqueous sodium hydroxide solution and evaporated to afford a solid residue that was recrystallized from a mixture of dichloromethane and acetonitrile to afford BDF1 in 70% isolated yield. A similar reaction with commercially available anisoin afforded BDF2 in excellent yield. It was noted that both BDF1 and BDF2 have limited solubility in dichloromethane, chloroform, benzene, or toluene. For example, BDF1 has a solubility of 30 mg/10 mL of CH\(_2\)Cl\(_2\) and BDF2 has a solubility of 40 mg/10 mL in CH\(_2\)Cl\(_2\). Hence, a readily soluble benzodifuran derivative BDF3 was also prepared by using 4,4′-dihexyloxybenzoin (Scheme 1), which in turn was obtained from anisoin by using standard procedures.\(^{(6)}\) The model diarylbenzofurans (M1-3) were obtained by a reaction of various benzoin derivatives with 3,4-dimethylphenol in excellent yields (Scheme 1).
Scheme 1. Preparation of Various BDFs and Model Compounds
The molecular structures of BDF1–3 and M1–3 were established with the aid of 1H/13C NMR spectroscopy and mass spectrometry, and further confirmed by X-ray crystallography (see the Supporting Information for the full experimental details).

With the various BDF derivatives at hand, we next examined their emission and excitation spectra in dichloromethane at 22 °C. The highly luminescent BDFs showed structured emission/excitation bands with a modest bathochromic shift going from the tetraphenyl derivative (i.e., BDF1) to the corresponding alkoxy-substituted derivatives (i.e., BDF2–3) (see Figure 2, left). In contrast, the model benzofuran derivatives (M1–3) showed only broad emission/excitation bands (see Figure 2, right).

![Figure 2. Comparison of the emission and excitation spectra of BDF1–3 (left) and M1–3 (right) in dichloromethane at 22 °C.](image)

The electron-donor strengths of various BDF derivatives and the initial indication of the stability of their cation radicals were evaluated by cyclic voltammetry. Thus, each benzodifuran and benzofuran derivative was subjected to electrochemical oxidation at a platinum electrode as a 2–3 mM solution in dichloromethane containing 0.1 M n-Bu4NPF6 as the supporting electrolyte. Figure 3 compiles the cyclic voltammograms of BDF1–3 (left) and benzofuran derivatives M1–3 (right). The benzodifuran derivatives, BDF1–3, showed two oxidation waves corresponding to the formation of monocation radicals and dications, respectively. The phenyl-substituted BDF1 showed that its first oxidation wave corresponding to the formation of the cation radical is completely reversible ($E_{ox1} = 1.17$ V vs SCE, see Figure 3, red curve) while the second oxidation to the dication occurs irreversibly (at ∼1.6 V vs SCE). Expectedly, the alkoxy-substituted BDF2 and -3 showed two reversible oxidation waves at very similar and relatively lower potentials (i.e., BDF2: 0.91 and 1.19; BDF3: 0.89 and 1.15 V vs SCE) as compared to the BDF1 owing to the presence of electron-donating alkoxy substituents. The cyclic voltammograms of the corresponding model benzofuran derivatives M1–3 showed at least one reversible oxidation wave occurring at relatively higher potentials (M1: 1.34 V vs SCE; M2: 1.0 V vs SCE; and M3: 1.04 V vs SCE) as compared to the corresponding BDF derivatives.
Figure 3. Comparison of the cyclic voltammograms of various benzodifuran (2 mM) and benzofuran (3 mM) derivatives in CH$_2$Cl$_2$ (0.1 M n-Bu$_4$NPF$_6$) at a scan rate of 200 mV s$^{-1}$. Note that the first oxidation wave of BDF1 is completely reversible (red curve) if the scanning is terminated before the start of the second oxidation event.

The electrochemical reversibility and relatively low oxidation potentials of benzodifuran and benzofuran derivatives prompted us to generate their cation radicals using a hydroquinone ether cation radical (MA$^{•+}$, $E_{\text{red}} = 1.11$ V vs SCE)$^7$ or a naphthalene cation radical (NAP$^{•+}$, $E_{\text{red}} = 1.34$ V vs SCE)$^8$ as stable (aromatic) one-electron oxidants.
Figure 4. Spectral changes upon the reduction of $1.3 \times 10^{-5}$ M NAP•+ by incremental addition of BDF1 in CH2Cl2 at 22 °C (left) and a comparison of the absorption spectra of BDF1•−3 cation radicals (middle) and M1−3 cation radicals (right).

Thus Figure 4 (left) shows the spectral changes attendant upon an incremental addition of substoichiometric amounts of BDF1 to a $1.3 \times 10^{-5}$ M NAP•+ ($\lambda_{\text{max}} = 672, 616, 503,$ and 396 nm; $\epsilon_{672} = 9300\, \text{M}^{-1}\, \text{cm}^{-1})$ in dichloromethane at 22 °C. Furthermore a plot of formation of the BDF1 cation radical (i.e., increase in the absorbance at 1100 nm) against the increments of added neutral BDF1 (see Figure S6 in the Supporting Information section) established that NAP•+ was completely consumed after the addition of 1 equiv of BDF1, and the resulting highly structured absorption spectrum of BDF1•+ [$\lambda_{\text{max}} = 502, 545, 610\,\text{(sh)},$ and 1100 (log $\epsilon = 3.81$) nm] remained unchanged upon further addition of neutral BDF1 (i.e., eq 1).

\[
\text{BDF1} + \text{NAP}^{++} \rightarrow \text{BDF1}^{++} + \text{NAP} \quad (1)
\]

Similarly, the cation radicals of various BDF and benzofuran derivatives were generated by using NAP•+ as well as MA•+ (see the Supporting Information section) and are compared in Figure 4. The absorption spectrum of BDF1•+ was expectedly similar to that of the alkoxy substituted BDF2•+ [$\lambda_{\text{max}} = 540\,\text{(sh)}, 572, 676,$ and 1368 (log $\epsilon = 4.37$) nm] and BDF3•+ [$\lambda_{\text{max}} = 541\,\text{(sh)}, 576, 705,$ and 1375 (log $\epsilon = 4.47$) nm] as shown in Figure 4 (middle). A compilation of the absorption spectra of the cation radicals of benzofurans M1•+ [$\lambda_{\text{max}} = 442, 720\,\text{(log $\epsilon = 3.74$),}$ and 950 nm], M2•+ [$\lambda_{\text{max}} = 478, 685\,\text{(sh)},$ 750 (log $\epsilon = 4.11$), and 1050 nm], and M3•+ [$\lambda_{\text{max}} = 480, 695\,\text{(sh)},$ 760 (log $\epsilon = 4.17$), and 1055 nm] in Figure 4 (right) shows that they contain similar spectral transitions, as in the spectra of the cation radicals of BDF derivatives. However, they lack the intense NIR transition (1180–1400 nm) that is attributed to a Robin Day III type intervalence transition in BDFcation radicals.$[9]$

The BDF cation radicals, obtained according to eq 1, are highly persistent at ambient temperatures and did not show any decomposition during a 24 h period at 22 °C, as confirmed by UV−vis spectroscopy. The single crystals
of the BDF1•+ and BDF2•+, suitable for X-ray crystallography, were obtained by a slow diffusion of toluene into the dichloromethane solutions of BDF1•+SbCl6− and BDF2•+SbCl6− at ~10 °C during the course of 2 days (see the Supporting Information).

The crystallographic analysis of the dark crystals of BDF1•+SbCl6− and BDF2•+SbCl6− revealed that they pack by the formation of translational stacks where peripheral α-aryl groups overlap with the central benzodifuran moieties of the neighboring molecules at a relatively large dihedral angle (~20°), see Figure 5.

Figure 5. The ORTEP diagrams showing the arrangement of BDF1•+SbCl6− (right) and BDF2•+SbCl6− (left) in unit cells.

A closer look at the bond length changes in the BDF cation radicals, together with a comparison of the corresponding neutral forms, the structures of which were established by X-ray crystallography, points to the following important observations: (i) The bond lengths in the central benzodifuran nuclei are identical in both BDF derivatives (see Table 1). (ii) In the cation radicals, the “olefinic” bonds (in the furan rings denoted e in the generic structure in Table 1) undergo increased delocalization with the central aromatic ring that leads to their elongation by ~3 pm and the shortening of adjacent bonds f and d by ~2 and ~3 pm, respectively (see Table 1). (iii) The central benzene ring acquires a quinoidal structure, i.e., bonds labeled b shorten by ~2 pm whereas the other four bonds (labeled a and c) become elongated by ~1 and ~2 pm, respectively. (iv) Interestingly, the structural changes (described above) in the benzodifuran moiety in BDF1•+ are roughly 1.5 times more pronounced than those in the case of BDF2•+ (see Table 1), and such a difference can be readily attributed to the fact that the unsubstituted phenyl groups in BDF1•+ are less involved in the stabilization of the positive charge as compared to the electron-rich p-anisyl groups in BDF2•+. For a complete listing of the bond lengths of the peripheral aryl groups in various structures, see Table S1 and S2 in the Supporting Information.
Table 1. Experimental and Theoretical Bond Lengths of the (Centrosymmetric) Neutral and Cation Radicals of BDF1 and BDF2 in Picometers (pm)

<table>
<thead>
<tr>
<th>bond</th>
<th>B3LYP/6-31G*</th>
<th>X-ray datab</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aBDF1</td>
<td>aBDF1++</td>
</tr>
<tr>
<td>a</td>
<td>140.3</td>
<td>141.8</td>
</tr>
<tr>
<td>b</td>
<td>138.5</td>
<td>137.1</td>
</tr>
<tr>
<td>c</td>
<td>141.6</td>
<td>142.6</td>
</tr>
<tr>
<td>d</td>
<td>144.8</td>
<td>142.0</td>
</tr>
<tr>
<td>e</td>
<td>137.7</td>
<td>141.1</td>
</tr>
<tr>
<td>f</td>
<td>138.4</td>
<td>136.7</td>
</tr>
<tr>
<td>g</td>
<td>136.8</td>
<td>137.1</td>
</tr>
<tr>
<td>h</td>
<td>146.3</td>
<td>144.5</td>
</tr>
<tr>
<td>i</td>
<td>147.8</td>
<td>147.3</td>
</tr>
</tbody>
</table>

|      | BDF2  | BDF2++ | Δ   | BDF2 | BDF2++ | Δ   |
| a    | 140.3  | 141.5   | +1.2 | 140.0(1)| 141.7(2)| +1.7 |
| b    | 138.5  | 137.3   | -1.2 | 138.1(1)| 136.5(2)| -1.6 |
| c    | 141.5  | 142.4   | +0.9 | 140.9(1)| 141.7(2)| +0.8 |
| d    | 144.8  | 142.5   | -2.3 | 144.7(1)| 141.7(2)| -3.0 |
| e    | 137.7  | 140.8   | +3.1 | 137.1(1)| 139.9(2)| +2.8 |
| f    | 138.5  | 137.2   | -1.3 | 138.6(1)| 137.3(2)| -1.3 |
| g    | 136.9  | 137.0   | +0.1 | 137.3(1)| 137.8(2)| +0.5 |
| h    | 146.1  | 144.0   | -2.1 | 145.9(1)| 144.3(2)| -1.6 |
| i    | 147.7  | 147.0   | -0.7 | 147.8(1)| 145.8(2)| -2.0 |

a Average bond lengths from two independent molecules.  
b Average esd for the bond lengths are shown in parentheses.

It is noteworthy that the α-aryl groups, which are more coplanar with the benzodifuran ring (να = 10–34°), undergo a pronounced quinoidal change owing to the delocalization of the cationic charge as compared to the less coplanar β-aryl groups (νβ = 44–61°) which show almost no change in their bond lengths (see Table S1 and S2 in the Supporting Information).

The experimental observations of the bond length changes in BDF cation radicals were found to be in reasonable agreement with the calculated values using DFT calculations at the B3LYP/6-31G* level (see Table 1). Furthermore, it is noted that the bonds which undergo the most dramatic lengthening (i.e., bonds a and e) and shortening (i.e., bonds b and d) in BDF cation radicals are the bonds on which the HOMO shows the largest bonding and antibonding character, respectively (i.e., Figure 6).
Figure 6. The HOMO’s of BDF1 (right) and BDF2 (left), obtained by DFT calculations at the B3LYP/6-31G* level.

In summary, we have demonstrated that various tetraarylbenzodifuran (BDF) and benzofuran derivatives can be easily prepared from readily available starting materials. These highly luminescent BDFs undergo reversible electrochemical oxidation and form stable cation-radical salts. The isolation and X-ray crystal structure determination of the neutral and cation radicals of BDF derivatives as well as the DFT calculations provide unequivocal evidence that a single charge (or polaron) in BDFs is stabilized largely by the benzodifuran and the α-aryl groups. Efforts are now underway to construct linear arrays of BDF derivatives to explore their conducting properties for potential applications in the emerging areas of molecular electronics and nanotechnology.\(^{(12)}\)

Acknowledgment

We thank the National Science Foundation (CAREER Award) for financial support.

References


7. Rathore, R.; Burns, C. L.; Deselnicu, M. I.; Denmark, S. E.; Bui, T. Org. Synth. 2005, 82, 1. Also see Figure S9 in the SI section.


10. Calculations were performed with the Spartan 06 software package.
