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# Synthesis, Electronic Properties, and X-ray Structural Characterization of Tetrarylbenzo[1,2-b:4,5-b']difuran Cation Radicals

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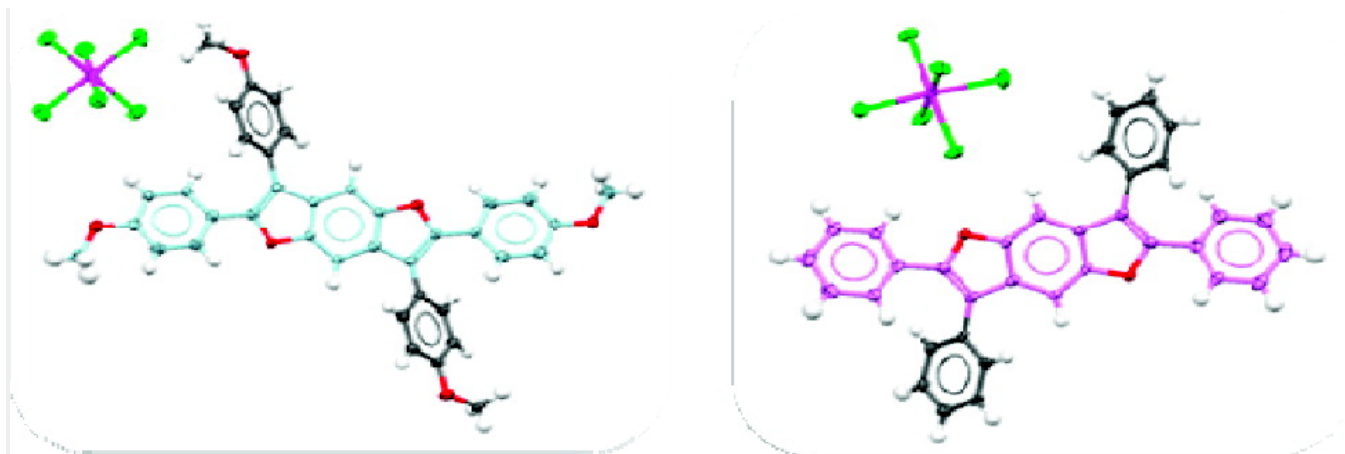
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## Abstract



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  $\alpha$ -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.<sup>(1)</sup> Tetraarylbenzo[1,2-*b*:4,5-*b'*]difurans (simply referred to hereafter as **BDF**), a largely unexplored<sup>(2, 3)</sup> 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).<sup>(4)</sup>

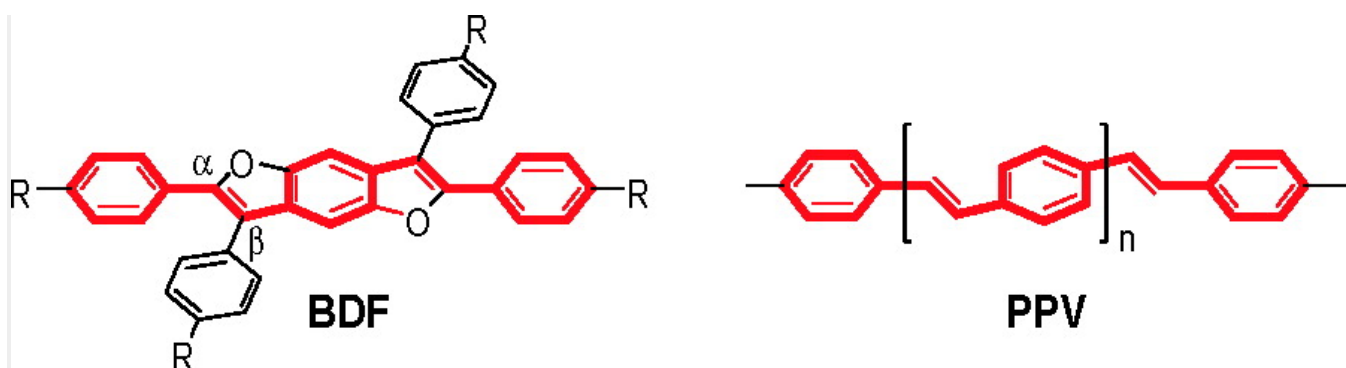


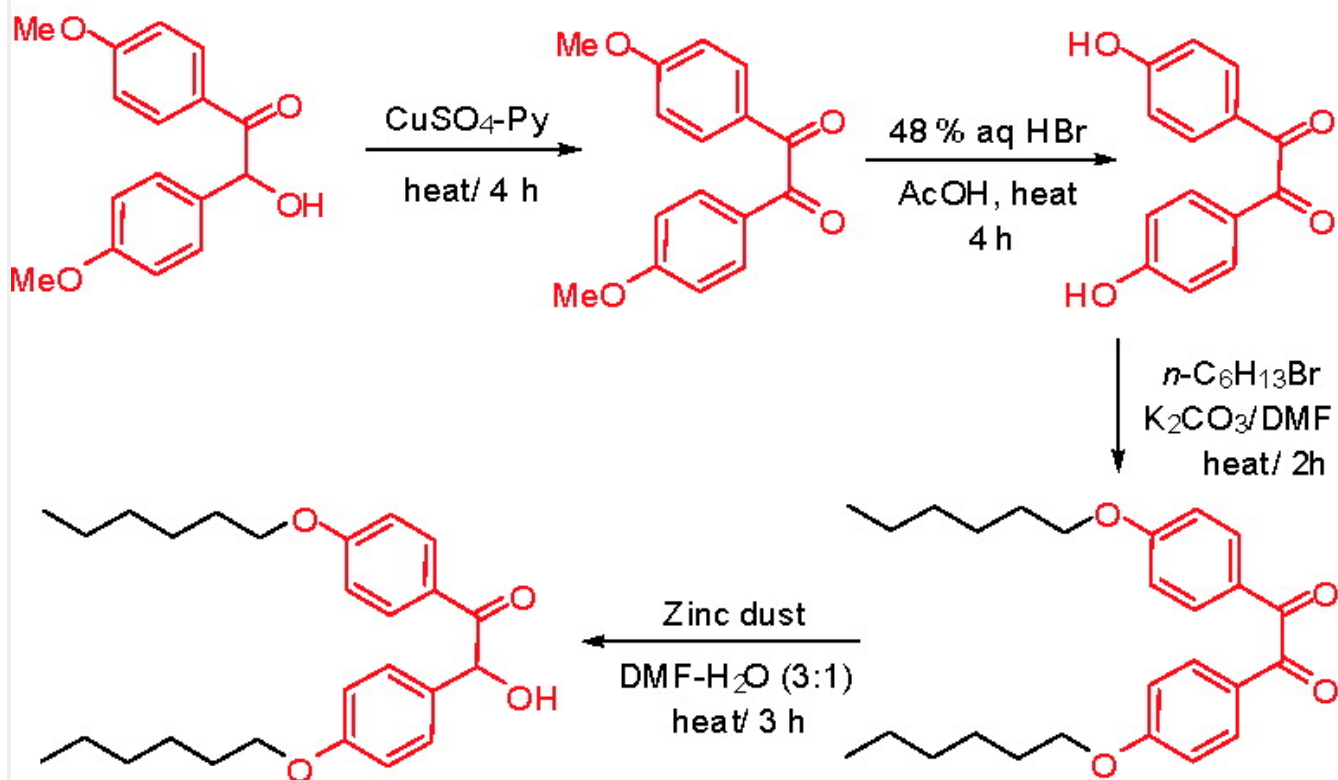
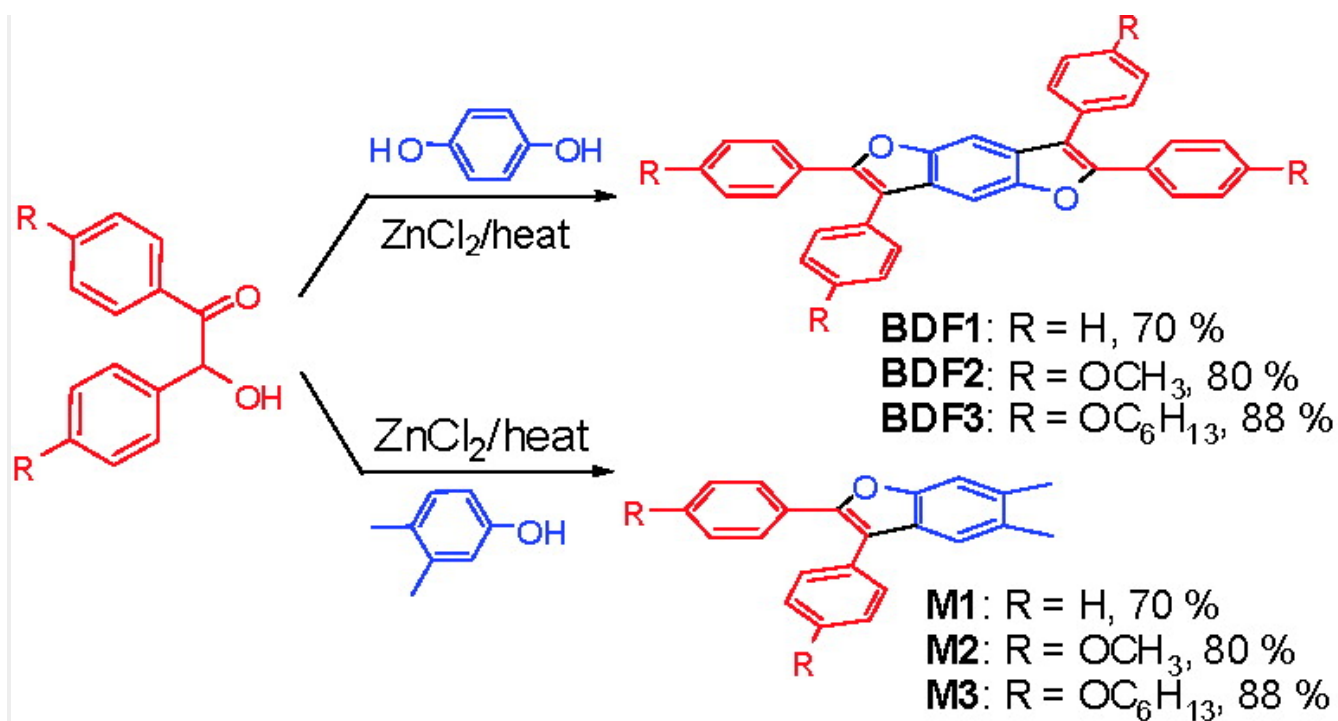
Figure 1. Structural similarities between polyphenylenevinylenes and tetraarylbenzo[1,2-*b*:4,5-*b'*]difurans.

Although **BDF** derivatives have been known for over a century<sup>(2)</sup> and can be easily prepared in excellent yields via Lewis acid-catalyzed condensations of benzoin or substituted benzoin with *p*-hydroquinone, their potential as electroactive materials has received little attention.<sup>(3)</sup>

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.<sup>(5)</sup>

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  $\alpha$ -aryl groups lying on the longitudinal axis (shown in red in Figure 1) while the  $\beta$ -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<sub>2</sub>Cl<sub>2</sub> and **BDF2** has a solubility of 40 mg/10 mL in CH<sub>2</sub>Cl<sub>2</sub>. 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.<sup>(6)</sup> 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  $^1\text{H}/^{13}\text{C}$  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).

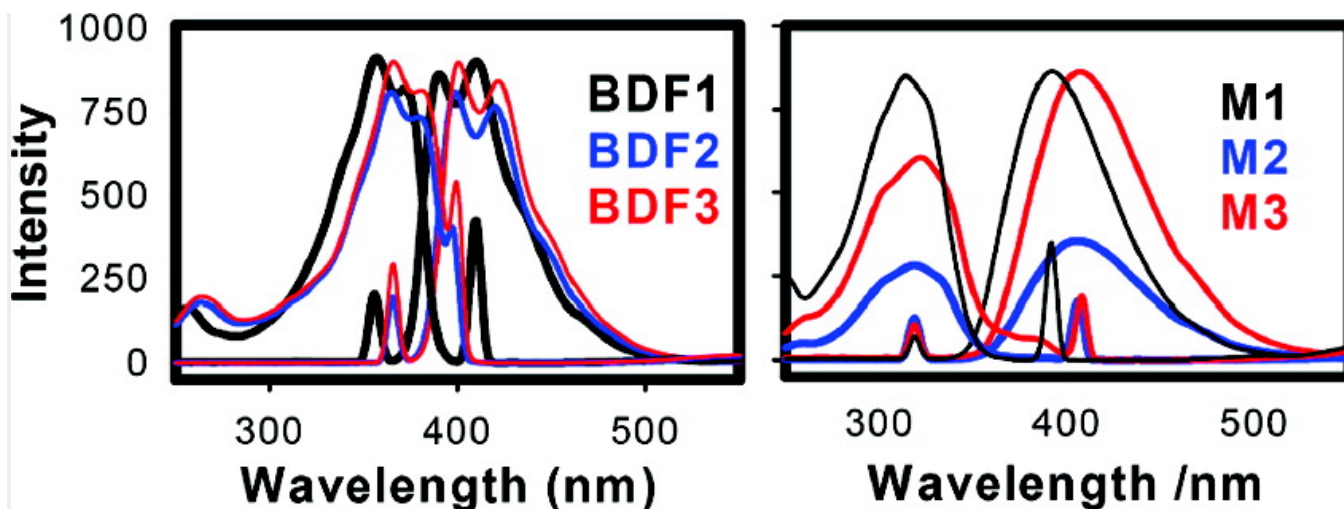


Figure 2. Comparison of the emission and excitation spectra of **BDF1–3** (left) and **M1–3** (right) in dichloromethane at 22 °C.

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  $n\text{-Bu}_4\text{NPF}_6$  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 dication, respectively. The phenyl-substituted **BDF1** showed that its first oxidation wave corresponding to the formation of the cation radical is completely reversible ( $E_{\text{ox1}} = 1.17$  V vs SCE, see Figure 3, red curve) while the second oxidation to the dication occurs irreversibly (at  $\sim 1.6$  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.

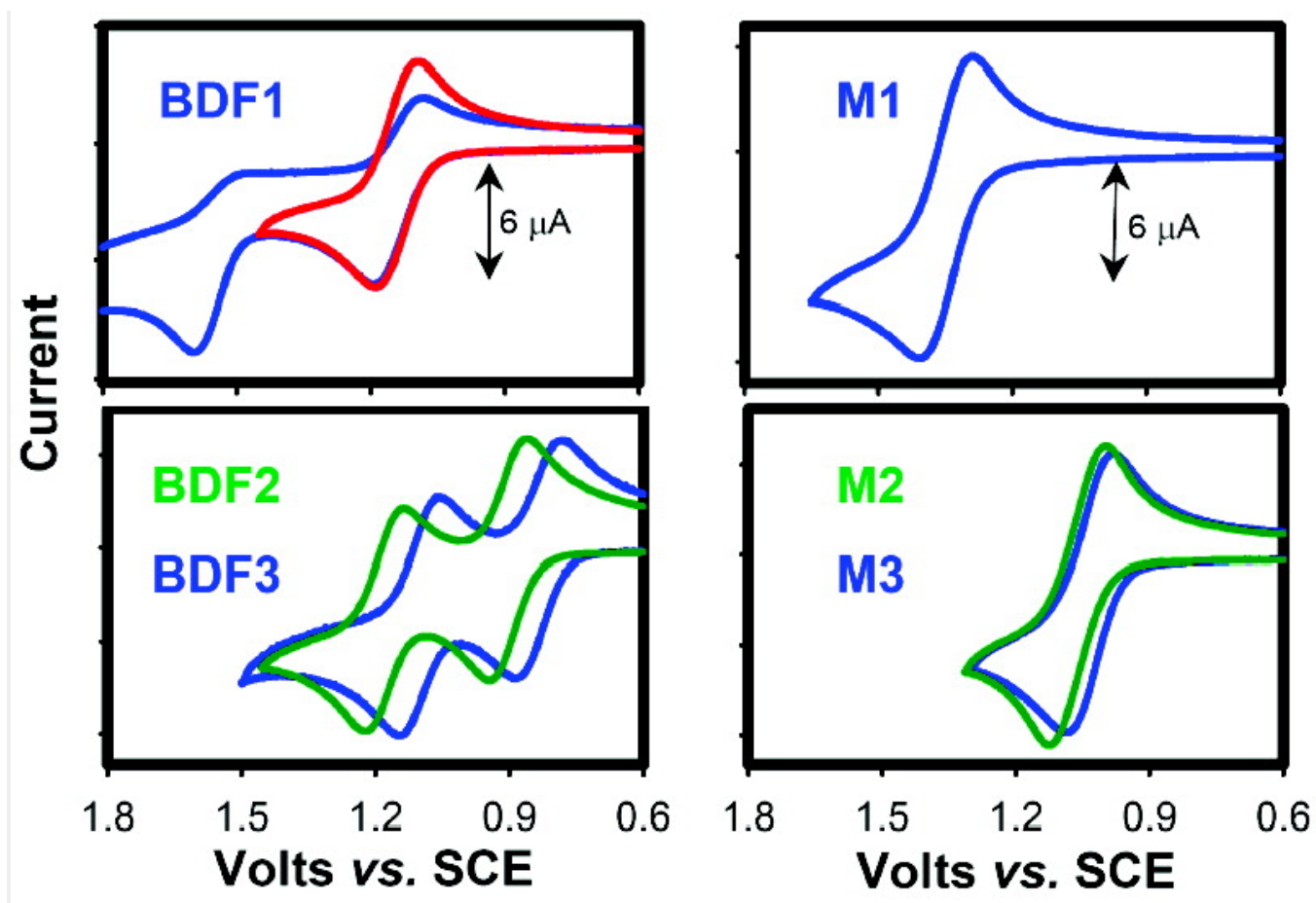


Figure 3. Comparison of the cyclic voltammograms of various benzodifuran (2 mM) and benzofuran (3 mM) derivatives in  $\text{CH}_2\text{Cl}_2$  (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>) at a scan rate of 200 mV s<sup>-1</sup>. Note that the first oxidation wave of **BDF1** is completely reversible (red 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 ( $\text{MA}^{\bullet+}$ ,  $E_{\text{red}} = 1.11$  V vs SCE)[\(7\)](#) or a naphthalene cation radical ( $\text{NAP}^{\bullet+}$ ,  $E_{\text{red}} = 1.34$  V vs SCE)[\(8\)](#) as stable (aromatic) one-electron oxidants.

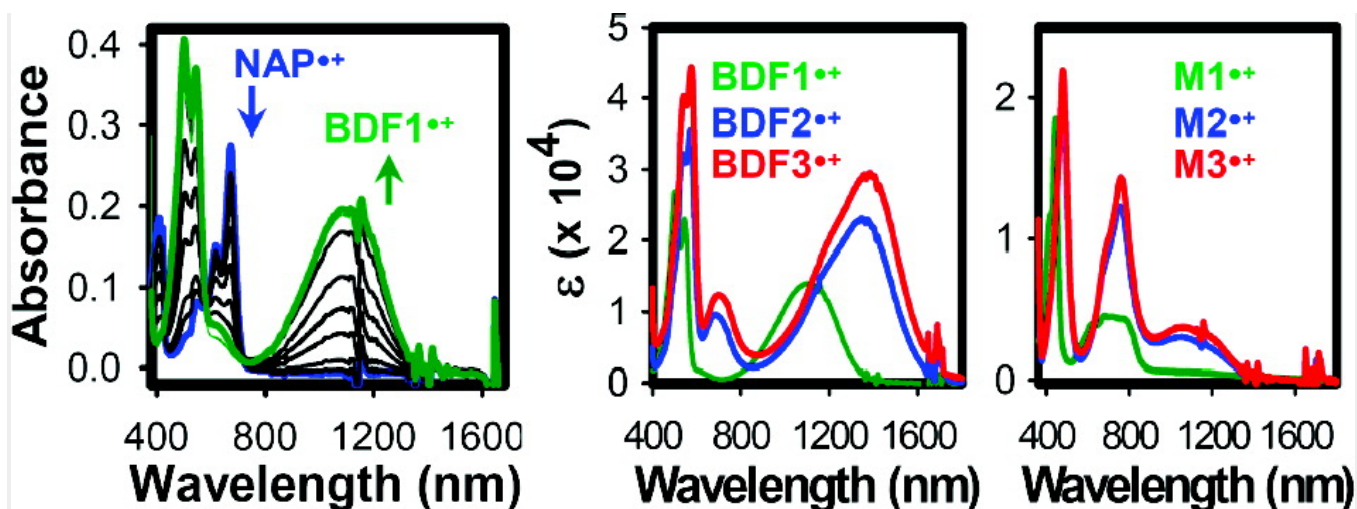
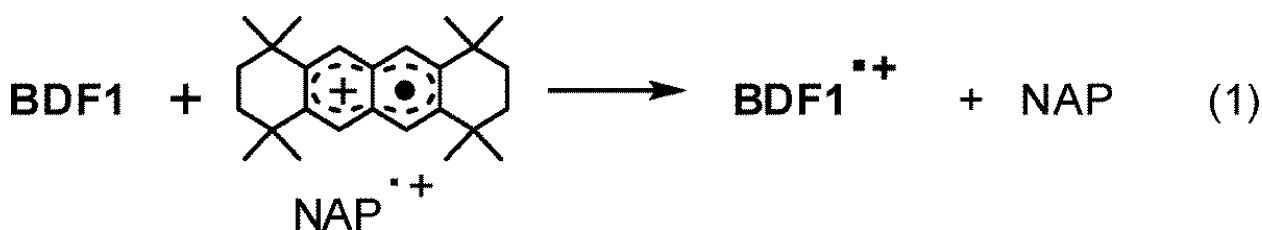


Figure 4. Spectral changes upon the reduction of  $1.3 \times 10^{-5}$  M  $\text{NAP}^{\bullet+}$  by incremental addition of **BDF1** in  $\text{CH}_2\text{Cl}_2$  at 22 °C (left) and a comparison of the absorption spectra of **BDF1–3** cation radicals (middle) and **M1–3** cation radicals (right).

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  $\text{NAP}^{\bullet+}$  ( $\lambda_{\text{max}} = 672, 616, 503,$  and  $396$  nm;  $\epsilon_{672} = 9300 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>(8)</sup> 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  $\text{NAP}^{\bullet+}$  was completely consumed after the addition of 1 equiv of **BDF1**, and the resulting highly structured absorption spectrum of **BDF1**<sup>•+</sup> [ $\lambda_{\text{max}} = 502, 545, 610$  (sh), and  $1100$  (log  $\epsilon = 3.81$ ) nm] remained unchanged upon further addition of neutral **BDF1** (i.e., eq 1).



Similarly, the cation radicals of various **BDF** and benzofuran derivatives were generated by using  $\text{NAP}^{\bullet+}$  as well as  $\text{MA}^{\bullet+}$  (see the [Supporting Information](#) section) and are compared in Figure 4. The absorption spectrum of **BDF1**<sup>•+</sup> was expectedly similar to that of the alkoxy substituted **BDF2**<sup>•+</sup> [ $\lambda_{\text{max}} = 540$  (sh), 572, 676, and 1368 (log  $\epsilon = 4.37$ ) nm] and **BDF3**<sup>•+</sup> [ $\lambda_{\text{max}} = 541$  (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**<sup>•+</sup> [ $\lambda_{\text{max}} = 442, 720$  (log  $\epsilon = 3.74$ ), and 950 nm], **M2**<sup>•+</sup> [ $\lambda_{\text{max}} = 478, 685$  (sh), 750 (log  $\epsilon = 4.11$ ), and 1050 nm], and **M3**<sup>•+</sup> [ $\lambda_{\text{max}} = 480, 695$  (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 **BDF**cation radicals.<sup>(9)</sup>

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**<sup>•+</sup> and **BDF2**<sup>•+</sup>, suitable for X-ray crystallography, were obtained by a slow diffusion of toluene into the dichloromethane solutions of **BDF1**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> and **BDF2**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> at -10 °C during the course of 2 days (see the [Supporting Information](#)).

The crystallographic analysis of the dark crystals of **BDF1**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> and **BDF2**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> revealed that they pack by the formation of translational stacks where peripheral  $\alpha$ -aryl groups overlap with the central benzodifuran moieties of the neighboring molecules at a relatively large dihedral angle ( $\sim 20^\circ$ ), see Figure 5.

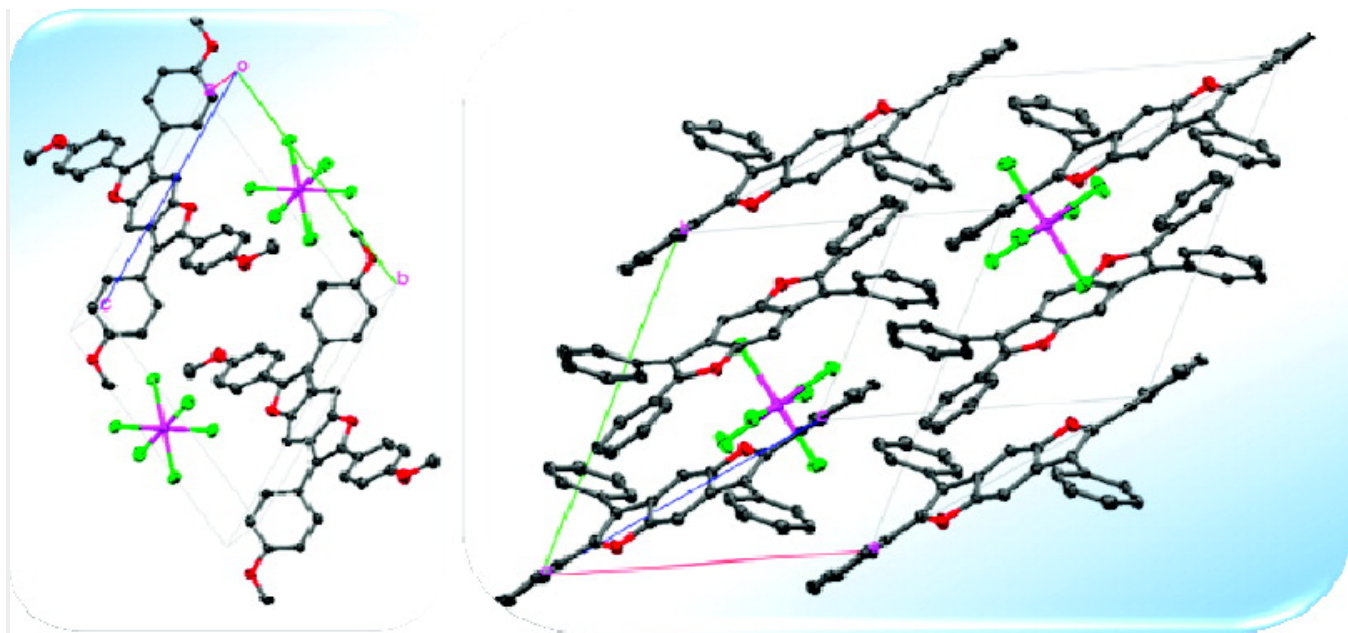
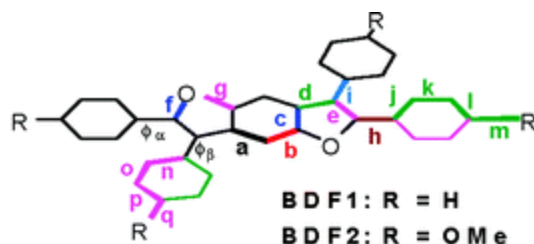


Figure 5. The ORTEP diagrams showing the arrangement of **BDF1**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (right) and **BDF2**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup> (left) in unit cells.

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  $\sim 3$  pm and the shortening of adjacent bonds **f** and **d** by  $\sim 2$  and  $\sim 3$  pm, respectively (see Table 1). (iii) The central benzene ring acquires a quinoidal structure, i.e., bonds labeled **b** shorten by  $\sim 2$  pm whereas the other four bonds (labeled **a** and **c**) become elongated by  $\sim 1$  and  $\sim 2$  pm, respectively. (iv) Interestingly, the structural changes (described above) in the benzodifuran moiety in **BDF1**<sup>•+</sup> are roughly 1.5 times more pronounced than those in the case of **BDF2**<sup>•+</sup> (see Table 1), and such a difference can be readily attributed to the fact that the unsubstituted phenyl groups in **BDF1**<sup>•+</sup> are less involved in the stabilization of the positive charge as compared to the electron-rich *p*-anisyl groups in **BDF2**<sup>•+</sup>. 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)**



bond	B3LYP/6-31G*			X-ray data <sup>b</sup>		
	<sup>a</sup> BDF1	<sup>a</sup> BDF1 <sup>++</sup>	$\Delta$	BDF1	BDF1 <sup>++</sup>	$\Delta$
a	140.3	141.8	+1.5	139.9(1)	142.2(5)	+2.3
b	138.5	137.1	-1.4	137.8(1)	135.3(5)	-2.5
c	141.6	142.6	+1.0	140.7(1)	142.1(5)	+1.4
d	144.8	142.0	-2.8	144.9(1)	141.6(5)	-3.3
e	137.7	141.1	+3.4	136.7(1)	140.3(5)	+3.6
f	138.4	136.7	-1.7	138.6(1)	136.7(4)	-1.9
g	136.8	137.1	+0.3	137.5(1)	137.9(4)	+0.4
h	146.3	144.5	-1.8	146.4(1)	144.9(5)	-1.5
i	147.8	147.3	-0.5	147.4(1)	147.5(5)	+0.1
	BDF2	BDF2 <sup>++</sup>	$\Delta$	BDF2	BDF2 <sup>++</sup>	$\Delta$
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  $\alpha$ -aryl groups, which are more coplanar with the benzodifuran ring ( $\nu_\alpha = 10\text{--}34^\circ$ ), undergo a pronounced quinoidal change owing to the delocalization of the cationic charge as compared to the less coplanar  $\beta$ -aryl groups ( $\nu_\beta = 44\text{--}61^\circ$ ) 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).<sup>(10)</sup> 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).<sup>(11)</sup>

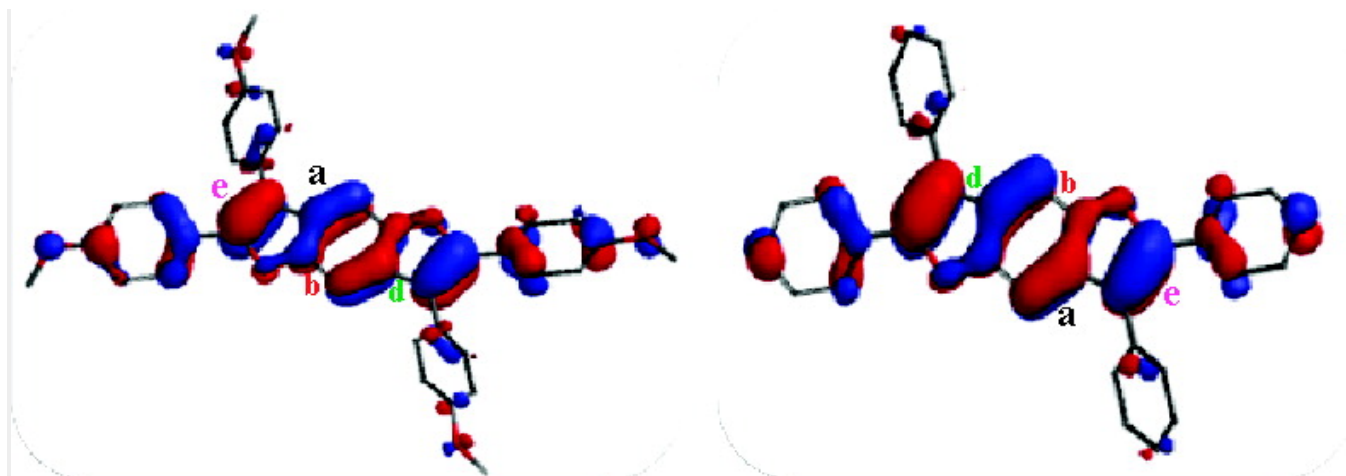


Figure 6. The HOMO's of **BDF1** (right) and **BDF2** (left), obtained by DFT calculations at the B3LYP/6-31G\* level.

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  $\alpha$ -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.<sup>(12)</sup>

## Acknowledgment

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