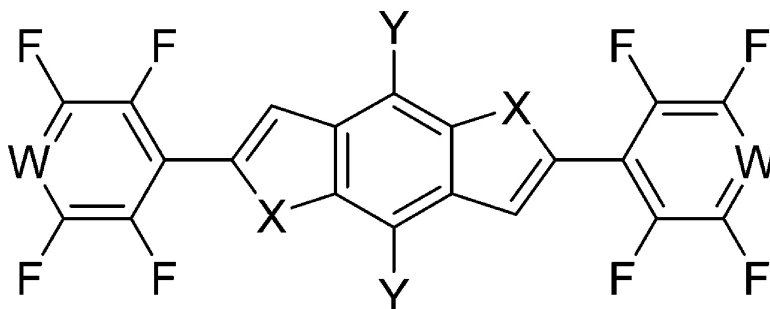


Benzodichalcogenophenes with Perfluoroarene Termini

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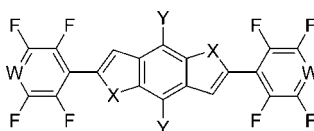
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ABSTRACT



Benzodichalcogenophenes are functionalized at their termini via S_NAr reactions of their bismetallates with perfluoroarenes. The identities of X, Y, and W are varied to study the effects on LUMO energy levels and crystallization motif. X-ray crystallography reveals that nearly all new derivatives crystallize with coplanar ring systems within slipped 1D or 2D π -stacks.

A number of fused aromatic polycyclics based on chalcogenophenes (i.e., thiophene and/or selenophene) have given good performance as organic semiconductors in various optoelectronic devices.¹ Specifically, benzodichalcogenophene (BDC) units are excellent building blocks for small molecule and polymeric semiconductors.² As for other π -systems, one may assume that their charge transport and device performance are largely affected by their crystallization motif, i.e., face-to-face or edge-to-face π -stacking. Face-to-face interactions can be favored via substituents around π -systems that preclude edge-to-face interactions.³ Arene–perfluoroarene (π – π F) interactions are increasingly employed to induce

face-to-face π – π packing.⁴ Another consequence is that n-channel behavior has been observed after introducing electron-withdrawing groups as terminal groups into p-type materials.^{2b,4b,5}

A series of BDCs terminated with electron-withdrawing benzenes and yielding electron mobilities as high as 0.1 cm^2/Vs in OFETs was reported.^{2b} Solid-state order of these materials was qualitatively assessed by X-ray diffraction of sublimed films. We provide here crystallographic studies of 9 out of 12 newly prepared BDC derivatives terminated by π F units to reveal their packing motifs. We hoped that the size mismatch between electron-rich BDC cores and smaller electron-poor terminal rings would cause each π -face to overlap with two other π -faces.⁶ Attractive interactions

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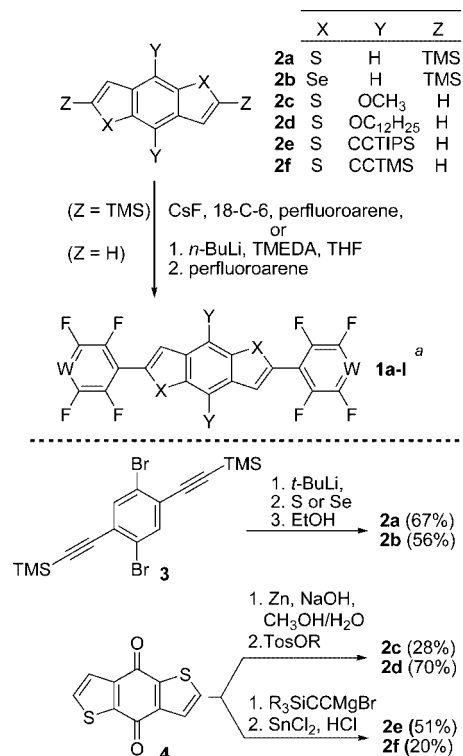
Table 1. Yields and Properties of BDC Derivatives **1**

	X	Y	W	yield (%)	λ_{\max}^a	λ_{\max}^b PL	Stokes shift	E_g^c (eV)	E_{red}^d onset (V)	LUMO ^e (eV)	HOMO ^f (eV)
					absorption peak/edge (nm)						
1a	S	H	CF	76	367/405	405	2557	3.1	-2.1	-2.7	-5.8
1b	S	H	CCF ₃	69	391/430	434	2534	2.9	-1.8	-3.0	-5.9
1c	Se	H	CF	65	385/418	<i>g</i>	<i>g</i>	3.0	-2.1	-2.7	-5.7
1d	Se	H	CCF ₃	56	408/446	<i>g</i>	<i>g</i>	2.8	-1.8	-3.0	-5.8
1e	S	O- <i>n</i> -C ₁₂ H ₂₅	CF	32	397/442	491	4822	2.8	-2.1	-2.7	-5.5
1f	S	O- <i>n</i> -C ₁₂ H ₂₅	CCF ₃	66	423/480	540	5122	2.6	-1.8	-3.0	-5.6
1g	S	OCH ₃	CF	47	392/440	498	5430	2.8	-2.1	-2.7	-5.5
1h	S	OCH ₃	CCF ₃	63	422/475	556	5711	2.6	-1.8	-3.0	-5.6
1i	S	CCTIPS	CF	60	406/440	437	1748	2.8	-1.8	-3.0	-5.8
1j	S	CCTIPS	CCF ₃	70	420/465	464	2258	2.7	-1.4	-3.4	-6.1
1k	S	CCTMS	CCF ₃	82	419/462	463	2268	2.7	-1.5	-3.3	-6.0
1l	S	OCH ₃	N	85	435/485	558	5078	2.6	-1.7	-3.1	-5.7

^a Solution absorption spectra (10⁻⁵–10⁻⁶ M THF). ^b Solution photoluminescence spectra (10⁻⁶–10⁻⁸ M THF). ^c Optical energy gap determined from the absorption edge. ^d Versus Fc/Fc⁺. ^e Estimated from reduction wave onset. (LUMO = -4.8 - E_{red}) ^f Estimated from HOMO = LUMO - E_g. ^g No observable PL.

between chalcogens and pendant fluorine atoms⁷ may contribute to coplanarization of their ring systems. The effects of substituents and core chalcogen atoms on frontier orbital energy levels were estimated by solution optical and electrochemical measurements. Although chalcogenophenes are typically coupled to fluorinated arenes via transition-metal-catalyzed coupling, a few examples^{7c,8} have exploited S_NAr chemistry of perfluoroarenes with metalated chalcogenophenes. This approach bypasses the need to first functionalize the chalcogenophene prior to coupling. We report here also the synthesis of a series of BDCs (**1**) with perfluoroarene termini, exploiting S_NAr chemistry.

BDC building blocks **2** were prepared by three separate routes. Silyl-functionalized **2a,b** were obtained after metal-halogen exchange of **3** with *t*-BuLi followed by adding chalcogen powder (sulfur or selenium).⁹ Isolated yields were diminished due to desilylation during flash chromatography. Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione **4** was prepared from 3-bromothiophene via a three-step published procedure.¹⁰ Reaction of **4** with alkynyl Grignard reagents and subsequent deoxygenation/aromatization with SnCl₂/HCl^{3b} yielded trimethylsilylacetylene (TMSA) and triisopropylsilylacetylene (TIPSA) functionalized **2e,f**. The low yield for **2f** relative to **2e** is again attributed to protodesilylation during flash chromatography. Reduction of **4** and in situ alkylation led to **2c/2d** bearing alkoxy groups.¹¹

Scheme 1. Synthesis of BDC Derivatives **1**

^aSee Table 1 for identities of W, X, and Y and isolated yields.

The aryl termini of previously reported 2,6-diaryl BDCs were introduced either in an early stage of the synthesis or in the final step by transitional-metal-catalyzed coupling, following a prerequisite functionalization step. S_NAr chemistry of 2,6-bismetalated BDCs with perfluoroarenes allows rapid access to a library of such derivatives. We employed two routes. The carbon-silicon bonds of **2a/b** were activated

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by a catalytic amount of fluoride and reacted with perfluoroarenes,^{8a} or the 2,6-positions of **2c–f** were lithiated with *n*-BuLi/TMEDA at $-78\text{ }^{\circ}\text{C}$ and quenched with perfluoroarenes. All BDCs **1** were isolated in analytically pure form after flash chromatography or in several cases after simple treatment with methanol.

Room temperature absorption and photoluminescence spectra of **1a–l** are included in Supporting Information (see Figure SI2), and relevant data are summarized in Table 1. All absorption spectra are broad and nearly featureless, indicating substantial freedom of rotation around the BDC- π F bonds. As noted for the parent diphenyl BDCs, replacement of S with Se causes a minor absorption red shift.¹² Most of the remaining differences in absorption λ_{max} and optical energy gaps (E_{g}), estimated from the onset of absorption, can be explained by tuning of the donor–acceptor type interaction between electron-rich BDC cores and electron-poor aryl termini. This behavior is exemplified by the series **1g** \rightarrow **1h** \rightarrow **1i**, bearing perfluorophenyl, perfluorotolyl, and perfluoropyridyl termini with λ_{max} values of 392, 422, and 435 nm. In agreement with a previous study of fluorinated π -systems,^{7a} replacement of terminal fluorines with CF_3 substituents reduces E_{g} through preferentially lowering LUMO energy by 0.3 eV. Alkoxy substituents destabilize the HOMO by resonance donation (mesomeric) but have little effect on the E_{g} via induction, thus inducing a red shift of 20–30 nm. Trialkylsilylacetylene substituents decrease the E_{g} by 0.2–0.3 eV (e.g., **1i/1j** vs **1a/1b**), similar to observed and calculated effects¹³ of these groups on pentacene. Estimation of frontier orbital energy levels via electrochemical measurements (see below) indicate that E_{g} is modulated by preferential stabilization of LUMO (trialkylsilyl acetylene, π F) or destabilization of HOMO (alkoxy) in a predictable fashion.

No detectable photoluminescence (PL) was observed for selenophene-based **1c** and **1d**. This contrasts optical studies¹² of the parent 2,6-diphenyl BDCs ($X = \text{S, Se, Te}$) where it was only the tellurophene derivative that exhibited no PL. For the remaining BDCs **1**, fairly systematic variation in Stokes shifts and PL fine structure suggest photoinduced intramolecular charge transfer states, modulated by electron-richness of the BDC core (donor) and electron-pooriness of the π F termini (acceptor).¹⁴ BDCs **1a, i, j, k** without electron-donating alkoxy substituents exhibit PL with moderate fine structure and Stokes shifts of 1750–2600 cm^{-1} . BDC **1i** with the least electron-withdrawing π F termini (C_6F_5) and trialkylsilylacetylene groups (inductively electron-withdrawing) on the donor yields the smallest Stokes shift and the most distinct fine structure. The Stokes shifts of BDCs with alkoxy substituents (greater donor–acceptor character) are approximately doubled in magnitude, and their PL profiles are nearly structureless. The discrepancy between the Stokes

shifts of **1f** and **1h** can only be possibly explained by greater aggregation of the latter.

The effects of substituents and core chalcogen atoms on LUMO energy levels of **1** were estimated from solution electrochemical measurements (Table 1). The identity of the chalcogen atom has little effect on LUMO level (**1c/1d** versus **1a/1b**).¹² However, the terminal and central substituents can significantly affect the LUMO. Alkoxy substituents exert little or no effect on LUMO levels, and therefore their effect on E_{g} is indeed due to destabilization of the HOMO. Replacement of terminal fluorine atoms ($W = \text{CF}$) with more electron-withdrawing CF_3 groups consistently lowers the LUMO level by 0.3–0.4 eV, in agreement with electrochemical studies of fluorinated heteroacenes.^{7a} LUMO levels are estimated to be -2.7 , -3.0 , and -3.1 eV for **1g**, **1h**, and **1i**, all bearing identical substituents on their BDC cores. Therefore, terminal perfluoropyridine rings ($W = \text{N}$) exert a stronger effect on the LUMO level than $W = \text{CCF}_3$. Substitution of the BDC core with trialkylsilyl acetylenes lowers LUMO levels by 0.3–0.4 eV compared to compounds with $Y = \text{H}$ (**1a** versus **1i, 1b** versus **1j** and **1k**). This and the effect of terminal CF_3 groups are additive here.

One goal here is to force the ring systems of BDCs **1** into coplanarity and enhance π -stacking, perhaps also leading to greater dimensionality of the π -stacks. Single-crystal X-ray analyses revealed that the ring systems of nearly all of the BDC derivatives **1a–1l** are coplanarized (Figure 1). The exception is **1a**, perturbed by intercalation of toluene solvent molecules into the π -stacks, demanding torsion (51°) between the BDC core and C_6F_5 rings to allow commensurate stacking distances. BDCs **1d** and **1k** crystallized in motifs similar to the others, but the diffraction data were of relatively low quality for small molecules and therefore not included. Suitable crystals could not be grown from **1c**.

Otherwise, all of the new BDCs **1** crystallize into face-to-face π -stacks with variable degrees of “pitch and roll”¹⁵ translation. Face-to-face stacking is enforced by π - π F interactions between overlapping perfluoroarene termini and BDC cores in all cases. All BDCs with CF_3 termini, regardless of the steric or electronic nature of Y , e.g., **1b** ($Y = \text{H}$), **1f** ($\text{OC}_{12}\text{H}_{25}$), **1h** (OCH_3), and **1j** (TIPSCC), pack in slipped stacks along only one dimension. Their CF_3 termini do not cause “large” increases in the π -stacking distance. The average distances between π -faces are 3.47 (**1b**), 3.37 (**1f**), 3.48 (**1h**), and 3.33 Å (**1j**). Compound **1e** without CF_3 groups also formed 1-dimensional slip stacks. Compound **1g** with $Y = \text{OCH}_3$ and $W = \text{CF}$ is one of only two new derivatives that forms slip π -stacks along two dimensions. One π -stacking axis is defined by four close contacts (C–S/C–C) per molecule and the other by four C–C close contacts. The average face-to-face (atom-to-plane) distance along one stacking axis is 3.33 Å and 3.47 Å along the other. The packing motif of **1i** might loosely be called a 2D π -stack. One stacking axis is defined by 14 C–C close contacts per molecule. Along the second axis, two carbons of the C_6F_5 rings approach those of others by 3.45 Å, which is slightly greater

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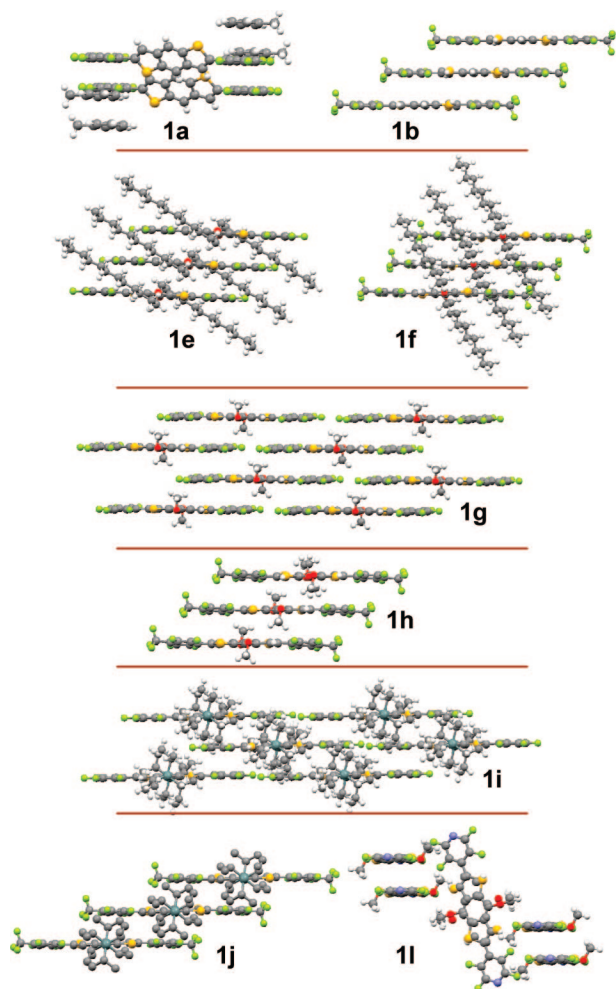


Figure 1. Crystal packing diagrams for BDC derivatives **1**.

than van der Waals radii. The average face-to-face (atom-to-plane) distance is 3.34 Å, and the closest C–C contact is only 3.27 Å.

All the BDC derivatives described above crystallize with edge-to-edge, but no edge-to-face, close contacts. The edge-to-face, herringbone-like packing motif of compound **1l** bearing terminal perfluoropyridine rings is unique among BDCs **1**. The molecular planes within one π -stack are inclined by 89° relative to the planes in adjacent stacks. Edge-to-face close contacts (N–F, S–F, and C–F) bridge adjacent oblique molecular planes. The π -stacking axis is defined by four C–C close contacts and two C–S close contacts per molecule, with the closest contact between 3.2 and 3.3 Å.

In summary, BDCs are easily functionalized with perfluoroarenes via S_NAr reactions as a final synthetic step. Electrochemical and optical measurements revealed that the positions and types of a discrete set of substituents affect E_g and LUMO levels in a consistent manner. Alkynyl substituents on the BDC core or CF_3 termini lower the E_g and LUMO level by approximately 0.2–0.3 eV, while terminal perfluoropyridines lower the LUMO further by 0.1 eV (**1l** vs **1h**). Solution optical measurements indicate intramolecular charge-transfer states with increasing bias of the donor–acceptor nature of this system. While face-to-face π -stacking of coplanar ring systems was achieved for nearly all new derivatives, no clear design principle for 2D π -stacking emerges as yet.

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Supporting Information Available: Synthesis and characterization details, crystallographic information file in CIF format, and absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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