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9,10-Disubstituted Octafluoroanthracene Derivatives via Palladium-Catalyzed Cross-Coupling

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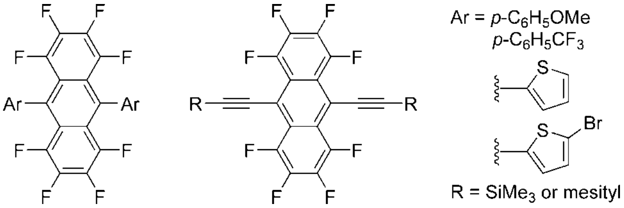

9,10-Dichlorooctafluoroanthracene (**1**) reacts with aryl boronic acids and terminal alkynes under palladium-catalyzed cross-coupling conditions to afford 9,10-diaryloctafluoroanthracenes (**2a**−**e**) and 9,10-dialkynyloctafluoroanthracenes (**6a**,**b**), respectively. Optical spectroscopy and cyclic voltammetry indicate that octafluoro-9,10-di(thiophen-2-yl)anthracene (**2d**) exhibits donor−acceptor character and a LUMO energy level of -3.27 eV relative to vacuum. A functionalized 5-bromothiophen-2-yl derivative (**2e**) was obtained in high yield by bromination of **2d** with NBS. X-ray crystallographic analysis of octafluoro-9,10-bis[(trimethylsilyl)ethynyl]anthracene (**6a**) reveals a solid-state structure that mimics the packing of columnar liquid crystals, with a π stacking distance of 3.39 Å between the octafluoroanthracene cores. In addition, octafluoro-9,10-bis(mesitylethynyl)anthracene (**6b**) displays a LUMO energy level of -3.50 eV, which approaches the value of -3.65 eV measured for perfluoropentacene, making 9,10-dialkynyloctafluoroanthracenes a promising new class of n-type organic materials.

Introduction

Progress in the field of organic electronics has enabled applications such as light-emitting diodes (LEDs),[1] field-effect transistors (FETs),[2] sensors,[3] and photovoltaics.[4] Because most organic compounds are inherently p-type (hole-transporting) semiconductors,[5] considerable research has focused on n-type (electron-transporting) materials for improved devices and complementary circuits.[6,7]

One strategy for affecting n-type behavior is the inclusion of electron-withdrawing groups, especially fluorine.[8] Suzuki et al. synthesized perfluoropentacene from tetrafluorophthallic anhydride and hydroquinone using Friedel−Crafts chemistry.[9] Fluorine substitution stabilizes the LUMO energy level of perfluoropentacene, leading to effective electron transport in both n-type FETs and bipolar devices with pentacene. Recently, Bao et al. measured an electron mobility of 0.72 cm^2 V^{-1} s^{-1} for *N*,*N*′-bis(heptafluorobutyl)-3,4:9,10-perylene diimide.[10] Cyclic voltammetry indicates a LUMO energy level of -3.85 eV for the partially fluorinated diimide, with n-type FETs that are stable in air for more than 50 days, presumably because of dense packing in the solid state.

Crystal engineering to afford extensive π stacking is well-established for p-type organic semiconductors.[11−14] Although

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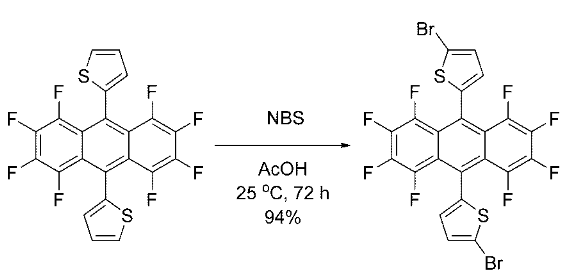
pentacene organizes into a herringbone pattern in the solid state, Anthony achieved a range of π-stacking motifs through alkynyl substituents.[11,12] Controlling the size and location of the alkyne functional groups gives 2-D "bricklayer" arrangements that exhibit high hole mobilities. However, there are few examples of crystal engineering for n-type or ambipolar acenes,[15] likely because of a lack of appropriate building blocks. For instance, with the exception of nucleophilic aromatic substitution,[16,17] synthetic methodology related to perfluoroacenes is limited.

To circumvent this problem, the optimized synthesis and preliminary C−C coupling chemistry of 9,10-dichlorooctafluoroanthracene (**1**) was reported.[18] Suzuki−Miyaura coupling of **1** with phenylboronic acid generated octafluoro-9,10-diphenylanthracene (**2a**) in 82% yield. Compound **2a** has a stabilized LUMO energy level of −3.04 eV and packs in the desired 2-D "bricklayer" structure.

This paper describes the reactivity of **1** with a variety of boronic acids and terminal alkynes under palladium-catalyzed cross-coupling conditions. To further assess **1** as a potential synthon for novel n-type organic semiconductors, the coupling products have been characterized by a number of methods, including UV−vis/fluorescence spectroscopy, cyclic voltammetry, and X-ray crystallography.

Results and Discussion

Synthesis of 9,10-Diaryloctafluoroanthracenes (2). Compound **1** was synthesized from commercially available tetrafluorophthallic acid and coupled with phenylboronic acid under modified Suzuki−Miyaura conditions[19] as previously described.[18] Similar conditions were applied in coupling reactions of **1** with a series of aryl boronic acids (Scheme 1). Compared to **2a**, the resulting 9,10-diaryloctafluoroanthracenes contain electron-donating (**2b**), electron-withdrawing (**2c**), and heteroaryl (**2d**) groups in order to probe substituent effects on the electronic properties and solid-state packing of the octafluoroanthracene core. Bromination of **2d** was also explored to provide synthetic handles for further C−C coupling chemistry (eq 1). Treatment of **2d** with excess NBS in glacial acetic acid at ambient temperature for 72 h afforded octafluoro-9,10-bis(5-bromothiophen-2-yl)anthracene (**2e**) in 94% yield.



2d **2e**

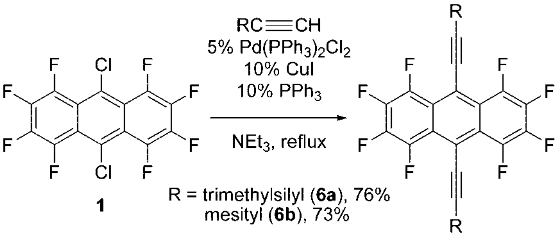
(1)

Repeated attempts to prepare the perfluorinated 9,10-diphenylanthracene, via coupling reactions with pentafluorophenylboronic acid, were unsuccessful. It appears that pentafluorophenylboronic acid is too electron deficient to transmetalate under these conditions.[19] Fagnou et al. overcame this issue by using palladium acetate, S-Phos,[19] and potassium carbonate to achieve efficient coupling between fluorinated aromatics and aryl halides,[20] but similar reactions between pentafluorobenzene and **1** exhibited minimal conversion.

Synthesis of Terminal Alkynes. Most of the terminal alkynes in this study are commercially available, while ethynylmesitylene was prepared as reported in the literature.[21] Synthesis of 5-ethynyl-5′-hexyl-2,2′-bithiophene (**4**) was accomplished by Sonogashira coupling[22] of 5-bromo-5′-hexyl-2,2′-bithiophene (**5**)[23] with ethynyltrimethylsilane, followed by deprotection under basic conditions (63% overall yield from **5**). Compound **4** degrades from a pale yellow powder to a brown solid over several days under ambient conditions, so it was stored in the dark under nitrogen and used promptly after purification.

Synthesis of 9,10-Dialkynyloctafluoroanthracenes (6). Ethynylbenzene and 1-ethynyl-4-methoxybenzene were initially chosen for Sonogashira coupling with **1**. Both reactions generated orange solids, and mass spectrometry indicated the presence of the desired 9,10-dialkynyloctafluoroanthracenes, but the limited solubilities of the two products precluded full characterization. Attempts to improve solubility by use of hexyl-substituted **4** as a coupling partner were unsuccessful and afforded an intractable dark green powder.

Fortunately, bulkier coupling partners gave soluble 9,10-dialkynyloctafluoroanthracenes in high yields under modified Sonogashira conditions (eq 2). The trimethylsilyl derivative **6a** is light-sensitive in solution and must be handled appropriately, and this hinders both the characterization of electronic properties and deprotection to the terminal dialkyne. However, octafluoro-9,10-bis(mesitylethynyl)anthracene (**6b**) was isolated as a stable, bright red solid in 73% yield.



(2)

Electronic Properties. The electronic properties of four new 9,10-disubstituted octafluoroanthracene derivatives were examined using optical spectroscopy and cyclic voltammetry. Each derivative was compared to **2a** to assess substituent effects on HOMO and LUMO energy levels, photoluminescence quantum yield, donor−acceptor character, and potential n-type behavior.

Optical data is compiled in Table 1, and representative UV−vis/fluorescence spectra of **2c** are shown in Figure 1. The 9,10-diaryloctafluoroanthracenes display C=C vibrational coupling,[24] while 9,10-dialkynyloctafluoroanthracene **6b** has one broad absorption band centered at 490 nm. Methoxyphenyl

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SCHEME 1. Synthesis of 9,10-Diaryloctafluoroanthracenes

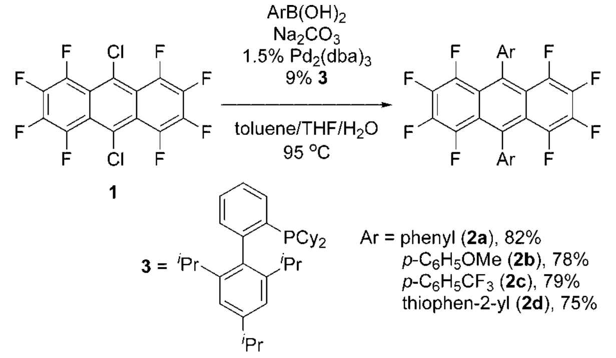

TABLE 1. Optical Data for 9,10-Disubstituted Octafluoroanthracene Derivatives

substituents	λ_{max}^{abs} (nm) in THF	λ_{max}^{em} (nm) in THF	λ_{max}^{em} (nm) in cyclohexane	E_g^{op} (eV)[a]	Φ_f[b]
phenyl (**2a**)[c]	377	441	438	3.00	0.12
p-C$_6$H$_5$OMe (**2b**)	379	458	442	2.94	0.04
p-C$_6$H$_5$CF$_3$ (**2c**)	377	439	439	2.99	0.41
thiophen-2-yl (**2d**)	388	*d*	*d*	2.89	0.00
mesitylethynyl (**6b**)	490	560	*e*	2.28	*e*

[a] E_g^{op} calculated from the onset of absorbance in THF. [b] Photoluminescence quantum yield determined in cyclohexane by comparison with 9,10-diphenylanthracene. [c] See reference 18. [d] Negligible fluorescence was observed in THF, cyclohexane, and chlorobenzene. [e] Not measured.

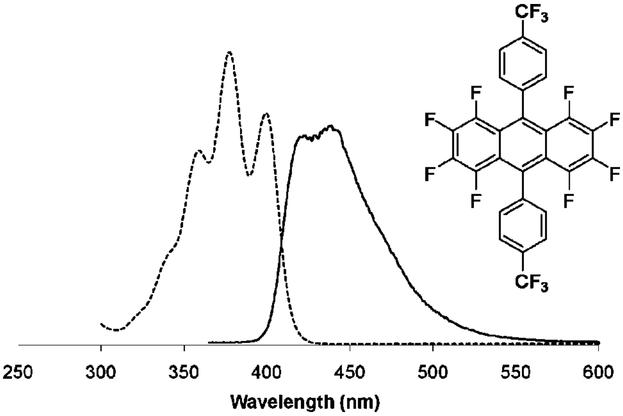

FIGURE 1. Absorbance (dashed line) and emission (solid line) spectra of **2c** in THF.

TABLE 2. Electrochemical Data for 9,10-Disubstituted Octafluoroanthracene Derivatives[a]

substituents	HOMO[b] (eV)	LUMO[b] (eV)	E_g^{el} (eV)
phenyl (**2a**)[c]	−5.93	−3.04	2.89
p-C$_6$H$_5$OMe (**2b**)	−5.82	−3.02	2.80
p-C$_6$H$_5$CF$_3$ (**2c**)	−6.02[d]	−3.14[e]	2.88
thiophene-2-yl (**2d**)	−5.88	−3.27	2.61
mesitylethynyl (**6b**)[f]	−5.70	−3.50[e]	2.20

[a] In acetonitrile, (Bu)$_4$NPF$_6$ electrolyte, Ag/AgNO$_3$ reference, 200 mV/s scan rate. [b] HOMO and LUMO energy levels (relative to vacuum) calculated from the onset of oxidation and reduction, respectively. [c] See ref 18. [d] Scan rate of 500 mV/s. [e] Scan rate of 50 mV/s. [f] In dichloromethane.

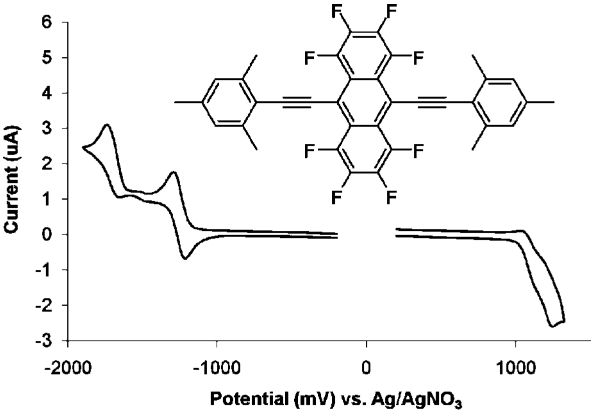

FIGURE 2. Cyclic voltammogram of **6b**.

derivative **2b** and thiophenyl derivative **2d**, with electron-donating substituents, exhibit smaller optical HOMO−LUMO energy gaps (E_g^{op}) of 2.94 and 2.89 eV, respectively. A substantially lower E_g^{op} of 2.28 eV is observed for **6b** because of extended conjugation.

Fluorescence spectroscopy of the 9,10-diaryloctafluoroanthracenes is consistent with donor−acceptor character in the excited state. Solvatochromism was measured by comparing fluorescence spectra in cyclohexane and THF (Table 1). Trifluorotolyl derivative **2c** has the same fluorescence maximum (λ_{max}^{em}) in both solvents, while the λ_{max}^{em} of **2b** undergoes a bathochromic shift of 18 nm in THF, suggesting a polarized excited state. Surprisingly, solvatochromism of **2d**, with the most electron-donating substituents, could not be measured because of negligible fluorescence. To ensure that aggregation was not quenching the emission, a fluorescence spectrum of **2d** was collected in chlorobenzene, and again no photoluminescence was detected. Increased donor−acceptor character is known to reduce photoluminescence quantum yields (Φ_f),[25] and this trend is reflected in the 9,10-diaryloctafluoranthracenes. Compound **2c** has a moderate Φ_f of 0.41, which decreases by an order of magnitude to 0.04 for **2b**, and no photoluminescence was observed for **2d**.

Cyclic voltammetry corroborated the E_g^{op} values and revealed substituent effects on the HOMO and LUMO energy levels. Electrochemical data is collected in Table 2, and a representative cyclic voltammogram of **6b** is shown in Figure 2. Compared to **2a**, trifluorotolyl groups, which are electron-withdrawing, stabilize both the HOMO and LUMO energy levels to the same extent (~0.1 eV), leading to minimal change in the electrochemical HOMO−LUMO energy gap (E_g^{el}). In contrast, methoxyphenyl substituents destabilize the HOMO energy level without affecting the LUMO energy level, creating a small decrease of 0.08 eV in E_g^{el}, but thiophenyl groups do not continue this trend. Compound **2d** has a slightly higher HOMO energy level, while the LUMO energy level is stabilized by 0.23 eV. Probably because of sterics, the thiophenyl subtituents seem to have better π overlap with the octafluoroanthracene core, thereby decreasing E_g^{el} to 2.61 eV.

The electrochemistry of 9,10-dialkynyloctafluoroanthracene **6b** is particularly interesting. Extended conjugation causes a significant decrease in E_g^{el} (down to 2.20 eV), and the HOMO energy level is moderately higher at −5.70 eV relative to vacuum. More importantly, compared to **2a**, the LUMO energy level is stabilized by 0.46 eV, and a second, irreversible reduction occurs at an onset potential of −1.58 V (Ag/AgNO$_3$ reference). The LUMO energy level of **6b** (−3.50 eV) is similar

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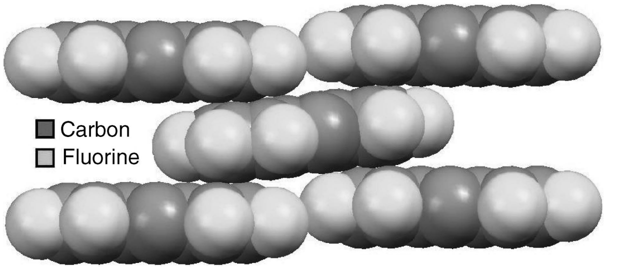

FIGURE 3. Space-filling view of the 2-D "bricklayer" structure in crystals of **2a**; phenyl groups removed for clarity (see ref 18).

to the value of -3.65 eV measured for perfluoropentacene,[9] making 9,10-dialkynyloctafluoroanthracenes promising candidates for n-type organic materials.

Solid-State Structure. Substituent effects on the packing of the octafluoroanthracene core were examined through X-ray crystallographic studies of **2b**, **2d**, and **6a**. Previously reported phenyl derivative **2a** exhibits the 2-D "bricklayer" structure associated with efficient charge transport (Figure 3).[11,12,18] Because of greater electron-density on the central anthracene ring, one might expect tighter π stacking for **2b** and **2d**, as has been observed in pentacene systems with enhanced donor−acceptor interactions between fluorinated and nonfluorinated rings.[26] However, the increased steric bulk of the methoxy groups in **2b** appears to disrupt the desired "bricklayer" structure, leading to herringbone packing with a tilt angle of 42° (Figure 4). Neighboring parallel molecules have a short interplanar distance of 3.1 Å, but significant translation (4.3 Å) along the short axis of the octafluoroanthracene core prevents π stacking.

As a heteroaryl analogue of **2a**, a 2-D "bricklayer" structure was anticipated for **2d**. Instead, thiophenyl derivative **2d** displays extended 1-D π stacking with an interplanar distance of 3.46 Å as shown in Figure 5. Slippage occurs in each π stack, with translational values of 5.3 and 0.6 Å down the long axis and short axis, respectively, of the octafluoroanthracene core. Adjacent π stacks are arranged in a herringbone pattern with a 75° tilt angle.

The alkynyl groups of **6a** seem to promote columnar π stacking of the molecules in the solid state. As shown in Figure 6, compound **6a** π stacks with a 1° tilt between octafluoroanthracene planes and a distance of 3.39 Å between the aromatic cores. When viewed down the *a*-axis (Figure 7), the rectangular face-centered cross-section resembles columnar liquid crystals (Col$_r$).[27,28] Each column has an alternating AB structure, with molecule B rotated about the *a*-axis by 52° relative to molecule A. Extended π stacks are insulated from neighboring columns by the alkynyl substituents, and solvent molecules (dichloromethane, $\sim$0.4 equiv) partially fill the remaining void space between columns. Nonfluorinated and partially fluorinated acene analogues, including those with similar size ratios between the alkyne functional group and the aromatic core,[29] do not exhibit this π-stacking motif, indicating that the electron-deficient octafluoroanthracene framework is important for columnar packing.[30]

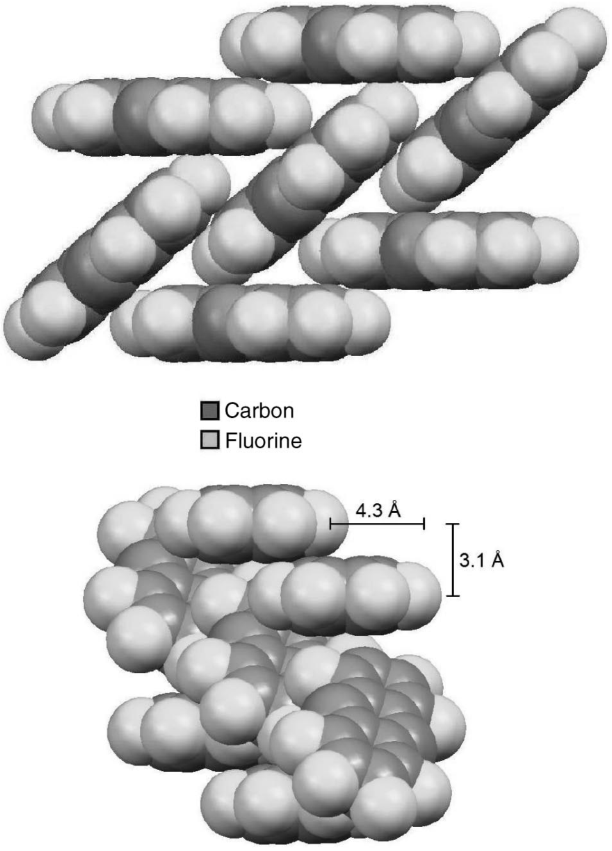

FIGURE 4. Two views of the crystal structure of **2b**; methoxyphenyl groups removed for clarity.

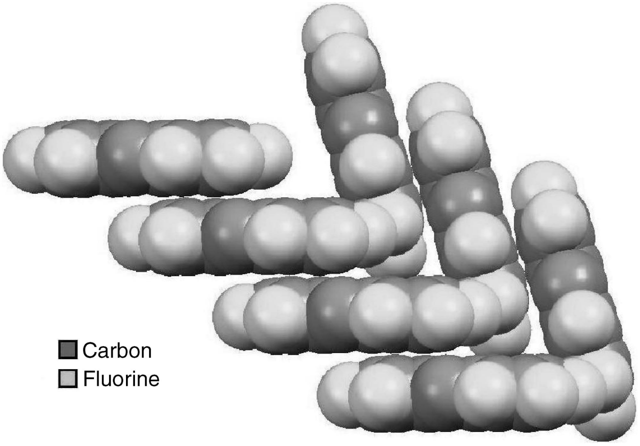

FIGURE 5. Space-filling view of the crystal structure of **2d**; thiophenyl groups removed for clarity.

Conclusion

9,10-Diaryloctafluoroanthracenes and 9,10-dialkynyloctafluoroanthracenes were synthesized from **1** using palladium-catalyzed cross-coupling, and initial structure−property relationships were probed. Recent literature has highlighted the advantages of donor−acceptor architectures for organic electronic applications, including small band gaps, broad absorption bands, balanced charge injection, and ambipolar transport.[25,31] Based on optical spectroscopy, compounds **1** and **2e** should

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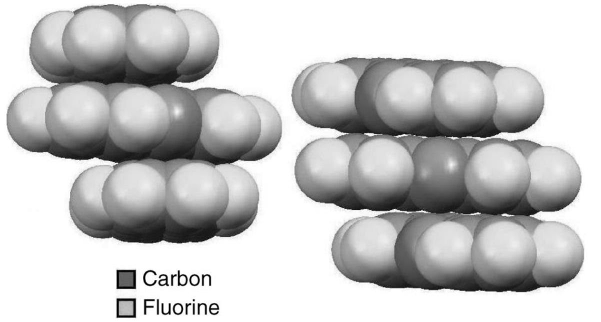

FIGURE 6. Space-filling view of the crystal structure of **6a**; alkynyl substituents and solvent molecules removed for clarity.

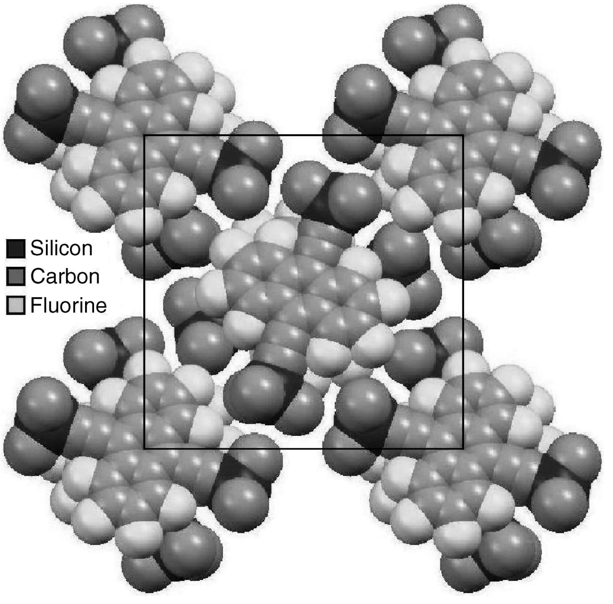

FIGURE 7. Space-filling view down the *a*-axis in crystals of **6a**; solvent molecules and hydrogen atoms removed for clarity.

provide synthetic access to new donor−acceptor oligomers and polymers. Moreover, the solid-state packing of **6a** is novel for linear acenes and warrants further studies on related molecules to discern the factors that direct this structural arrangement. Both the synthesis and device performance of a range of 9,10-dialkynyloctafluoroanthracenes are currently being explored, as the stabilized LUMO energy levels and columnar π stacking of these compounds could lead to high-performance n-type organic materials. Future efforts will also involve attempts to obtain oligomers and polymers via cross-coupling with dichloride **1**. In addition, dibromide **2e** is expected to provide a range of donor−acceptor structures through straightforward coupling reactions.

Experimental Section[32]

1,2,3,4,5,6,7,8-Octafluoro-9,10-bis(4-methoxyphenyl)anthracene (2b). Phosphine **3** (0.03 g, 0.06 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.01 g, 0.01 mmol), sodium carbonate (0.21 g, 2.00 mmol), 4-methoxyphenylboronic acid (0.30 g, 2.00 mmol), and **1** (0.30 g, 0.77 mmol) were loaded into a flask in a glovebox. A degassed mixture of toluene (3 mL), THF (3 mL), and water (1 mL) was transferred via cannula onto the solids, and the resulting solution was stirred under reflux at 95 °C for 13 h. The crude product was extracted with chloroform and washed with aq $NaHCO_3$. The organic layer was passed through a plug of silica gel (hexanes eluant) and then concentrated under vacuum to give a pale yellow solid. Slow cooling of a toluene solution gave 0.32 g (78%) of yellow crystals. Mp (DSC): 326 °C. ^{1}H NMR: δ 7.29 (d, J = 9 Hz, 4 H), 7.01 (d, J = 9 Hz, 4 H), 3.93 (s, 6 H). ^{19}F NMR: δ −135.4 (d, J = 13 Hz, 4 F), −156.4 (d, J = 13 Hz, 4 F). GC−MS (EI) *m*/*z*: 534 (M^+). Anal. Calcd for $C_{28}H_{14}F_8O_2$: C, 62.93; H, 2.64. Found: C, 62.93; H, 2.53.

1,2,3,4,5,6,7,8-Octafluoro-9,10-bis[4-(trifluoromethyl)phenyl]anthracene (2c). The procedure for **2b** was repeated with 4-(trifluoromethyl)phenylboronic acid (0.38 g, 2.00 mmol) and a reaction time of 12 h. Slow cooling of an ethanol solution gave 0.37 g (79%) of yellow crystals. Mp (DSC): 299−300 °C. ^{1}H NMR: δ 7.76 (d, J = 8 Hz, 4 H), 7.53 (d, J = 8 Hz, 4 H). ^{19}F NMR: δ −63.7 (s, 6 F), −134.2 (d, J = 13 Hz, 4 F), −154.5 (d, J = 13 Hz, 4 F). GC−MS (EI) *m*/*z*: 610 (M^+). Anal. Calcd for $C_{28}H_8F_{14}$: C, 55.10; H, 1.32. Found: C, 54.90; H, 1.38.

1,2,3,4,5,6,7,8-Octafluoro-9,10-di(thiophen-2-yl)anthracene (2d). The procedure for **2b** was repeated with 2-thiophenylboronic acid (0.25 g, 2.00 mmol) and a reaction time of 18 h. Slow cooling of a hexanes solution gave 0.28 g (75%) of yellow crystals. Single crystals for X-ray diffraction were obtained by slow evaporation of a chloroform-*d*/dichloromethane/pentane solution. ^{1}H NMR: δ 7.57 (dd, J = 5 and 1 Hz, 2 H), 7.18 (dd, J = 5 and 4 Hz, 2 H), 7.12 (dd, J = 4 and 1 Hz, 2 H). ^{19}F NMR: δ −137.3 (d, J = 12 Hz, 4 F), −154.7 (d, J = 12 Hz, 4 F). GC−MS (EI) *m*/*z*: 486 (M^+). Anal. Calcd for $C_{22}H_6F_8S_2$: C, 54.32; H, 1.24; S, 13.18. Found: C, 54.49; H, 1.20; S, 12.99.

1,2,3,4,5,6,7,8-Octafluoro-9,10-bis(5-bromothiophen-2-yl)anthracene (2e). Compound **2d** (0.04 g, 0.08 mmol) and NBS (0.07 g, 0.39 mmol) were stirred in glacial acetic acid (10 mL) under ambient conditions for 48 h. A second portion of NBS (0.07 g, 0.39 mmol) was added, and the reaction was stirred for an additional 24 h. The resulting yellow solution was quenched with water (100 mL) and ether (15 mL). The organic layer was washed with water and then passed through a plug of silica gel (hexanes eluant). Concentration under vacuum gave 0.05 g (94%) of a yellow solid. Mp: 253−255 °C. ^{1}H NMR: δ 7.12 (d, J = 4 Hz, 2 H), 6.86 (d, J = 4 Hz, 2 H); ^{19}F NMR: δ −136.7 (d, J = 12 Hz, 4 F), −153.7 (d, J = 12 Hz, 4 F). MS (FAB) *m*/*z*: 644 (M^+). Anal. Calcd for $C_{22}H_4Br_2F_8S_2$: C, 41.02; H, 0.63; S, 9.96. Found: C, 40.86; H, 0.27; S, 9.62.

5-Ethynyl-5′-hexyl-2,2′-bithiophene (4). Triphenylphosphine (0.06 g, 0.23 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.08 g, 0.11 mmol), copper(I) iodide (0.04 g, 0.23 mmol), and **5**[23] (1.25 g, 3.80 mmol) were loaded into a flask under positive nitrogen pressure. Degassed triethylamine (40 mL) was transferred via cannula onto the solids, followed by addition of ethynyltrimethylsilane (0.47 g, 4.75 mmol). A condenser was attached, and the resulting solution was stirred under reflux for 12 h. The crude product was extracted with hexanes and washed successively with ammonium chloride, water, and brine. The organic layer was passed through a plug of silica gel (hexanes eluant) and then concentrated under vacuum. Trimethylsilyl groups were removed by stirring for 4 h with aq KOH (0.40 g, minimal water) in methanol (40 mL). The resulting terminal alkyne was extracted with ether and washed with water and brine. Concentration of the organic layer afforded a tan solid that was recrystallized from hexanes to give 0.66 g (63%) of pale yellow powder. This product degrades to a brown solid over several days under ambient conditions, so it was used promptly after purification. ^{1}H NMR (C_6D_6): δ 6.90 (d, J = 4 Hz, 1 H), 6.78 (d, J = 4 Hz, 1 H), 6.65 (d, J = 4 Hz, 1 H), 6.39 (d, J = 4 Hz, 1 H), 2.94 (s, 1 H), 2.49 (t, J = 8 Hz, 2 H), 1.47 (m, 2 H), 1.09−1.27 (m, 6 H), 0.86 (t, J = 7 Hz, 3 H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.7, 23.3, 29.4, 30.7, 32.17, 32.21, 77.6, 83.0, 120.9, 123.3, 124.9, 125.7, 134.60, 134.66, 140.5, 146.7. GC−MS (EI) *m*/*z*: 274 (M^+).

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(32) See the Supporting Information for general experimental details.

(33) Compound **3a** is light-sensitive in solution, so it must either be purified quickly or handled in the dark. Yellow needles of **3a** are stable indefinitely under ambient conditions.

Anal. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37. Found: C, 69.82; H, 6.71; S, 23.59.

1,2,3,4,5,6,7,8-Octafluoro-9,10-bis[(trimethylsilyl)ethynyl]anthracene (6a).[33] Triphenylphosphine (0.02 g, 0.08 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.03 g, 0.04 mmol), copper(I) iodide (0.02 g, 0.08 mmol), and **1** (0.30 g, 0.77 mmol) were loaded into a flask under positive nitrogen pressure. Degassed triethylamine (10 mL) was transferred via cannula onto the solids, followed by addition of ethynyltrimethylsilane (0.19 g, 1.92 mmol). A condenser was attached, and the resulting solution was stirred under reflux for 16 h. The crude product was extracted with ether and washed successively with ammonium chloride, water, and brine. The organic layer was passed through a plug of silica gel (hexanes eluant) and then concentrated under vacuum. Slow cooling of a hexanes solution gave 0.30 g (76%) of fine yellow needles. Single crystals for X-ray diffraction were obtained by slow evaporation of a dichloromethane/pentane solution. ^{1}H NMR: δ 0.34 (s, 9 H). ^{19}F NMR: δ −137.2 (d, J = 13 Hz, 4 F), −154.7 (d, J = 13 Hz, 4 F). GC−MS (EI) m/z: 514 (M$^+$). Anal. Calcd for $C_{24}H_{18}F_8Si_2$: C, 56.02; H, 3.53. Found: C, 55.73; H, 3.56.

1,2,3,4,5,6,7,8-Octafluoro-9,10-bis(mesitylethynyl)anthracene (6b). The procedure for **6a** was repeated using ethynylmesitylene[21] (0.14 g, 0.96 mmol) and stirring under reflux for 24 h. The crude product was extracted with chloroform and washed successively with ammonium chloride, water, and brine. The organic layer was passed through a plug of silica gel (hexanes eluant) and then concentrated under vacuum. Slow cooling of a toluene/methanol solution gave a bright red solid (0.17 g, 73%). Mp: 266−267 °C. ^{1}H NMR: δ 6.95 (s, 4 H), 2.53 (s, 12 H), 2.34 (s, 6H). ^{19}F NMR: δ −137.7 (d, J = 14 Hz, 4 F), −155.5 (d, J = 14 Hz, 4 F). HRMS (EI): calcd for $C_{36}H_{22}F_8$ 606.1594 (M$^+$), found 606.1588.

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Supporting Information Available: General experimental, UV−vis/fluorescence spectra of **2b**, **2d**, and **6b**, cyclic voltammograms of **2b**−**d**, NMR spectra of new compounds, and crystallographic data for **2b**, **2d**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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