JOC*Article*

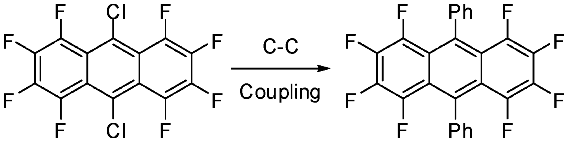
9,10-Dichlorooctafluoroanthracene as a Building Block for n-Type Organic Semiconductors

John F. Tannaci, Masahiro Noji,[†] Jennifer McBee, and T. Don Tilley*

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

tdtilley@berkeley.edu

Received February 27, 2007



9,10-Dichlorooctafluoroanthracene (**1**) was synthesized from commercially available tetrafluorophthalic acid by an optimized solution-phase route. To establish **1** as a synthon for n-type organic semiconductors, the compound was reacted with phenylboronic acid under modified Suzuki−Miyaura coupling conditions to generate octafluoro-9,10-diphenylanthracene (**7**) in high yield. Cyclic voltammetry and X-ray crystallography indicate that **7** has a stabilized LUMO energy level and exhibits extended π stacking, which should lead to efficient electron transport in solid-state devices. 1,2,3,4,5,6,7,8-Octafluoroanthracene (**2**) was also synthesized as a potential n-type building block, but suitable C−C coupling conditions for this compound were not found, and **2** could not be converted into 9,10-dibromooctafluoroanthracene or octafluoro-9,10-diiodoanthracene.

Introduction

Organic semiconductors are an active area of research driven by potential applications that include light-emitting diodes,[1] photovoltaics,[2] and field-effect transistors (OFETs).[3] Many conjugated organic systems have inherently low electron affinities and therefore behave as p-type semiconductors and as hole-transport materials.[4] Improved electron-transport (n-type) materials are generally needed to develop more efficient devices and to enable other cost-effective applications such as complementary circuits.[5]

Electron-deficient heterocycles have been investigated as n-type materials,[6] and related π systems that feature fluorine substituents have also been examined.[7,8] Fluorine substitution lowers LUMO energy levels, increases stability for devices operating under ambient conditions,[7] and can lead to donor−acceptor interactions that direct extensive π stacking in the solid state.[9] Marks et al. have inserted perfluorophenyl groups into oligothiophenes to obtain vapor-deposited OFETs with high electron mobilities (up to 0.43 cm^2 V^{-1} s^{-1}, $I_{on}/I_{off} > 10^8$).[8]

Extended perfluoroacenes are a potentially useful class of efficient electron-transport materials. These compounds retain many of the attractive physical properties of the parent hydrocarbons due to the small size difference between fluorine and hydrogen. For example, pentacene is one of the most effective p-type organic semiconductors,[10] and Suzuki et al. have reported the related isostructural perfluoropentacene.[11] Fluorine substitution dramatically lowers the LUMO energy level to −3.65 eV (relative to vacuum) and thereby enables fabrication of n-type OFETs. The thin-film *d*-spacing of perfluoropentacene remains similar to that of pentacene (15.8 and 15.4 Å, respectively), which apparently results in good electrical contacts when both materials are layered to form bipolar OFETs.

[†] Current address: Meiji Pharmaceutical University, 2-522-1, Noshio, Kiyose, Tokyo 204-8588, Japan.

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(3) Sun, Y.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 53.

(4) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969.

(5) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H. E.; Li, W. *Nature* **2000**, *403*, 521.

(6) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

(7) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787.

(8) Yoon, M.-H.; Facchetti, A.; Stern, C. E.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 5792.

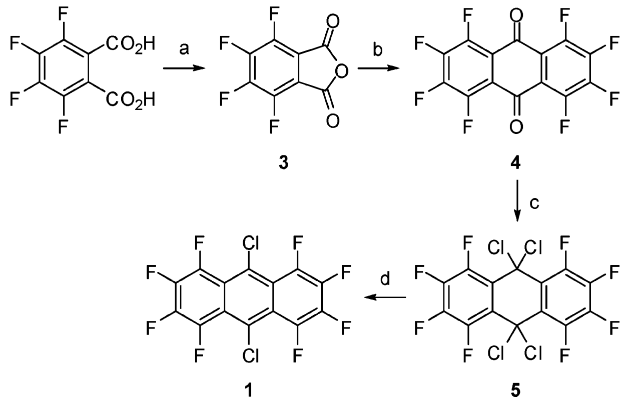
(9) Reichenbächer, K.; Süss, H. I.; Hulliger, J. *Chem. Soc. Rev.* **2005**, *34*, 22.

(10) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W. *J. Appl. Phys.* **2002**, *92*, 5259.

(11) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.

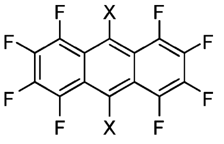
10.1021/jo070404a CCC: $37.00

SCHEME 1. Synthesis of 9,10-Dichlorooctafluoroanthracene[a]



[a] Key: (a) $SOCl_2$, 90 °C, 14 h, 97%; (b) CsF, sulfolane/*m*-xylene (3:5), 160 °C, 30 min, 59%; (c) PCl_5, phenylphosphonic dichloride, 170 °C, 24 h, 83%; (d) glacial AcOH, NMP, 115 °C, 24 h, 85%.

Besides nucleophilic aromatic substitution[12,13] few methods exist for adding conjugated units to perfluoropentacene and shorter, related homologues like perfluoroanthracene. Replacing some of the fluorine atoms in perfluoroanthracene with functional handles for C−C coupling should provide ideal building blocks for novel n-type materials. To that end, this paper describes the synthesis and preliminary C−C coupling chemistry of 1,2,3,4,5,6,7,8-octafluoroanthracene derivatives **1** and **2**. The fluorinated compounds are fully characterized, and their electronic properties are probed by UV−vis/fluorescence spectroscopy and cyclic voltammetry. The solid-state structures have also been investigated.

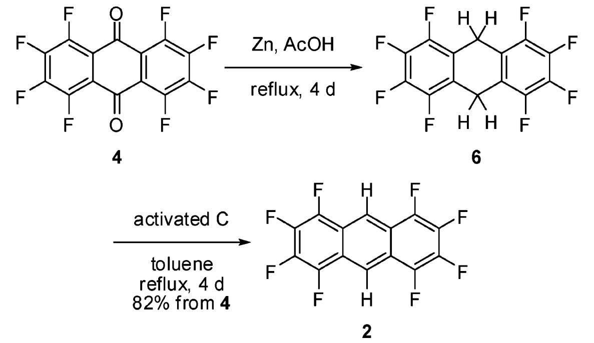


1: X = Cl
2: X = H

Results and Discussion

Synthesis of 9,10-Dichlorooctafluoroanthracene (1). Compound **1** was synthesized in four steps from tetrafluorophthalic acid as shown in Scheme 1. The commercially available starting material was reacted with thionyl chloride at 90 °C for 14 h to give tetrafluorophthalic anhydride (**3**) in 97% yield.[14,15] Subsequent formation of 1,2,3,4,5,6,7,8-octafluoroanthraquinone (**4**)[16−18] was achieved by fluoride-promoted decarboxylation and dimerization of **3**. Chlorination of **4** with a combination of phosphorus pentachloride and phenylphosphonic dichloride proceeded smoothly at 170 °C to generate 9,9,10,10-tetrachlorooctafluoro-9,10-dihydroanthracene (**5**) in 83% yield.[19] The final aromatization was induced by heating **5** to 115 °C in the presence of acetic acid.

SCHEME 2. Synthesis of 1,2,3,4,5,6,7,8-Octafluoroanthracene



Synthesis of 1,2,3,4,5,6,7,8-Octafluoroanthracene (2). The synthesis of **2** from **4** was accomplished in two steps as shown in Scheme 2. Zinc dust in boiling acetic acid was used as the reducing agent,[20] and 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydroanthracene (**6**) was collected after ether extraction. This crude product was stirred under air with activated carbon[21] in refluxing toluene for 4 days to give **2** in 82% overall yield from **4**. No reaction occurred in the absence of activated carbon, and using a pure oxygen atmosphere led to overoxidation. Also, standard dehydrogenation reagents such as chloranil and DDQ were ineffective at aromatizing **6** to **2**.

Synthesis of Octafluoro-9,10-diphenylanthracene (7). Phenylboronic acid was chosen as the initial coupling partner to investigate **1** as a building block for n-type materials. Although the aryl chloride is activated by electron-withdrawing groups, standard Suzuki−Miyaura reaction conditions[22] led to minimal coupling. Improved reactivity was observed using bulky, electron-rich tri-*tert*-butylphosphine as a ligand,[23] but coupling was slow and incomplete. The best results were obtained with tris(dibenzylideneacetone)dipalladium(0) in the presence of commercially available phosphine **8**,[24] which efficiently catalyzed the coupling of **1** with phenylboronic acid (2.6 equiv) (Scheme 3). The reaction was found to be quantitative by ^{19}F NMR spectroscopy, and workup followed by recrystallization gave an 82% yield of **7**.

Optimization of 1,2,3,4,5,6,7,8-Octafluoroanthraquinone Synthesis. Compound **4** is typically produced in one step from tetrachlorophthalic anhydride and excess potassium fluoride.[16−18] At high temperatures (≥300 °C) halide substitution occurs in combination with the fluoride-promoted decarboxylation and dimerization. Such harsh conditions are not ideal for lab-scale synthesis, so modifications were made to enable a solution-phase reaction at lower temperature. Halide substitution was circumvented by using **3** instead of tetrachlorophthalic anhy-

---

(12) Geramita, K.; McBee, J.; Shen, Y.; Radu, N.; Tilley, T. D. *Chem. Mater.* **2006**, *18*, 3261.

(13) Nitschke, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 10183.

(14) Gething, B.; Patrick, C. R.; Tatlow, J. C. *J. Chem. Soc.* **1960**, 1574.

(15) Okumara, Y.; Ito, H.; Kaieda, O. Preparation of Fluorine-Containing Phthalic Anhydride Derivatives. Jpn. Kokai Tokkyo Koho JP 06016656, 1994.

(16) Yakobson, G. G.; Odinokov, V. N.; Vorozhtsov, N. N., Jr. *Tetrahedron Lett.* **1965**, *49*, 4473.

(17) Burdon, J.; Childs, A. C.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 534.

(18) Kaieda, O.; Hirota, K.; Itoh, H.; Awashima, M.; Nakamura, T. Fluorinated Quinones. Eur. Pat. Appl. EP 170190, 1986.

(19) Takebe, Y.; Murobuse, H.; Okazoe, T.; Kashiwagi, T.; Tamura, M. Preparation of 9,9,10,10-Tetrachloro-9,10-dihydroanthracenes. Jpn. Kokai Tokkyo Koho JP 11012203, 1999.

(20) Lu, L.; Chen, Q.; Zhu, X.; Chen, C. *Synthesis* **2003**, *16*, 2464.

(21) Nakamichi, N.; Kawabata, H.; Hayashi, M. *J. Org. Chem.* **2003**, *68*, 8272.

(22) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 41−123.

(23) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176.

(24) Billingsley, K. L.; Anderson, K. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 3484.

SCHEME 3. Coupling Conditions for 9,10-Dichlorooctafluoroanthracene

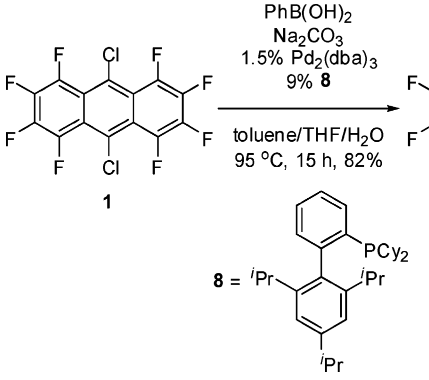


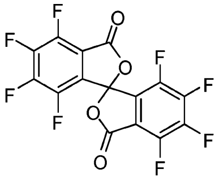
TABLE 1. Optimization of 1,2,3,4,5,6,7,8-Octafluoroanthraquinone Synthesis[a]

run	time (h)	solvent	yield[b] (%)
1	2	DMF/*m*-xylene	40
2	3	NMP/*m*-xylene	48
3	4	DMSO/*m*-xylene	3
4	0.5	sulfolane/*m*-xylene	59

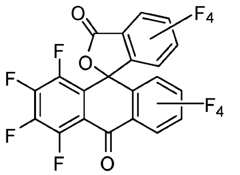
[a] CsF, **3**, 160 °C. [b] Yield of **4** after sublimation and recrystallization.

dride, and cesium fluoride was used to improve fluoride solubility and activity.

Preliminary attempts to synthesize **4** in *m*-xylene at 160 °C gave dilactone **9** as the major product. Dilactone **9** has previously been postulated as an intermediate in this type of reaction,[16] and here full characterization, including structure confirmation by X-ray crystallography,[25] is reported. Decarboxylation of **9** was favored by increasing the polarity of the solvent system (DMF/*m*-xylene, 3:5), giving **4** in 40% yield after sublimation and recrystallization. Analysis of the sublimation residue revealed substantial formation of lactone **10**, which may have been produced by trimerization of **3** followed by rearrangement,[26] although a more likely pathway is reaction of **4** with additional starting material.[27]



9



10

Substituting other polar solvents for DMF can significantly affect the yield of **4**, so optimization studies were performed as shown in Table 1. Interestingly, DMSO (run 3) drastically lowered the isolated yield of **4**. Use of sulfolane/*m*-xylene as a solvent system (run 4) led to a shortened reaction time and maximum yield (59%) of the desired compound.

Optimization of 9,10-Dichlorooctafluoroanthracene Synthesis. Aromatization of **5** to **1** (Table 2) based on reported conditions[28] (runs 1 and 2) was not selective, and mixtures including unreacted starting material (**5**), the desired product (**1**), 9-chloro-1,2,3,4,5,6,7,8-octafluoroanthracene (**11**), and **2** were formed. Attempts to boost activity by using Rieke zinc[29] (runs 3−6) were promising, but the reactions required freshly prepared metal reagents and gave variable results. Zinc dust in 1-methyl-2-pyrrolidinone/acetic acid (NMP/AcOH, 3:1) at 110 °C was overly reducing, as it afforded **6** as the sole product in 92% isolated yield (run 7). Fortunately, acetic acid in NMP at elevated temperatures (run 8) was sufficient to cleanly aromatize **5** to **1**.

Attempted Reactions of 1,2,3,4,5,6,7,8-Octafluoroanthracene. Recently, Fagnou et al. reported efficient coupling between aryl halides and fluorinated aromatics using palladium acetate, S-Phos,[30] and potassium carbonate in isopropyl acetate.[31] For example, mesityl bromide was reacted with pentafluorobenzene to give 2,3,4,5,6-pentafluoro-2′,4′,6′-trimethylbiphenyl in 98% yield. Unfortunately, these conditions were ineffective in coupling bromobenzene with **2**.

Halogenation of **2** was also attempted under a wide variety of conditions, but neither 9,10-dibromooctafluoroanthracene nor octafluoro-9,10-diiodoanthracene was observed. Direct halogenation using several brominating or iodinating agents gave no reaction, and deprotonation/halogenation routes using alkyllithium reagents led to multiple side products. Piers et al. encountered similar problems while trying to brominate fluorinated binaphthyl derivatives.[32] These issues were overcome by using LTMP as a base at low temperature in the presence of tributyltin chloride (Bu_3SnCl) as a quenching electrophile. The resulting aryltin species was subsequently converted to the desired compound. However, exposing **2** to LTMP/Bu_3SnCl at −78 °C returned the starting material, and allowing the reaction to warm to higher temperatures gave an uncharacterized mixture of products.

Electronic Properties. To investigate the electronic properties of the octafluoroanthracene derivatives, compounds **1**, **2**, and **7** were characterized by UV−vis/fluorescence spectroscopy and cyclic voltammetry. The parent hydrocarbons (anthracene, 9,10-dichloroanthracene, and 9,10-diphenylanthracene) were studied under the same conditions to allow proper comparisons between fluorinated and non-fluorinated analogues.

Solution-phase optical data is collected in Table 3, and representative UV−vis/fluorescence spectra of **7** are shown in Figure 1. All six compounds exhibit coupling in the absorbance spectra due to C═C vibrational modes,[33] but the fluorinated materials have broader peaks that obscure some of the fine vibronic structure. Fluorine substitution on the anthracene core does not dramatically affect the optical HOMO−LUMO energy gap leading to a small bathochromic shift in the onset of absorbance (≤0.14 eV). With regard to fluorescence, only anthracene and 9,10-dichloroanthracene show sharp vibronic coupling, with absorbance and emission spectra that display distinct mirror symmetry. The fluorinated compounds exhibit broad peaks in the fluorescence spectra as well as Stokes shifts that are approximately 10 nm larger than those of the non-fluorinated analogues.

---

(25) See Supporting Information for crystallographic data.

(26) Yamato, T.; Sakaue, N. *J. Chem. Res. Synop.* **1997**, 440.

(27) Carissimo-Rietsch, F.; Schmitz, C.; Aubry, J.-M. *Tetrahedron Lett.* **1991**, *32*, 3845.

(28) Takebe, Y.; Murofushi, H.; Okazoe, T.; Kashiwagi, K.; Tamura, M. Preparation of 9,10-Dihaloanthracenes. Jpn. Kokai Tokkyo Koho JP 11012204, 1999.

(29) Wu, X.; Rieke, R. D. *J. Org. Chem.* **1995**, *60*, 6658.

(30) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685.

(31) Lafrance, M.; Shore, D.; Fagnou, K. *Org. Lett.* **2006**, *8*, 5097.

(32) Morrison, D. J.; Riegel, S. D.; Piers, W. E.; Parvez, M.; Mcdonald, R. *Chem. Commun.* **2006**, 2875.

(33) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press Inc.: New York, 1965.

TABLE 2. Optimization of 9,10-Dichlorooctafluoroanthracene Formation[a]

reaction conditions					^{19}F NMR molar ratio[b]				
run	Zn source	solvent	temp (°C)	additive	**5**	**1**	**11**	**2**	**6**
1	Zn	DMF	25	DBE[c]	89	11			
2	Zn/ZnCl$_2$	MeOH	25		14	20	57	9	
3	Rieke Zn	THF	25		6	86 (74)	8		
4	Rieke Zn	MeOH	25		55	7	14	24	
5	Rieke Zn	NMP	25			100 (91)			
6	Rieke Zn	DMF	25		49	12	33	6	
7	Zn	NMP	110	AcOH					100 (92)
8		NMP	115	AcOH		100 (85)			

[a] From **5**. [b] Isolated yields in parentheses. [c] 1,2-Dibromoethane.

TABLE 3. Optical Data for Anthracene Derivatives[a,b]

compound	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	E_g^{op} (eV)
anthracene[c]	357	402	3.24
9,10−dichloroanthracene[c]	380	431	2.99
9,10−diphenylanthracene[c]	373	408	3.05
2	359	412	3.17
1	394	458	2.85
7	377	441	3.00

[a] In THF. [b] E_g^{op} calculated from the onset of absorbance. [c] Consistent with published values (see ref 33).

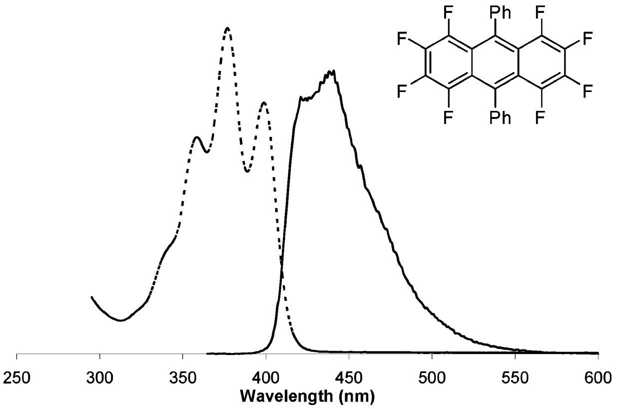


FIGURE 1. Normalized absorbance (dashed line) and emission (solid line) spectra of **7** in THF.

To examine electronic interactions in the solid state, UV−vis measurements were also conducted on thin films of **1** and **7**.[34] Films were drop cast from dichloromethane (1 mg/mL, glass substrate) and were found to be of low quality by optical microscopy. Repeated attempts to improve film quality through spin casting, thermal annealing, or solvent-vapor annealing were unsuccessful. Relative to solution-phase absorbance, both compounds display thin-film bathochromic shifts of 10 nm as well as low-energy shoulders. These features indicate increased electronic delocalization even in low-quality films, presumably through intermolecular $\pi-\pi$ interactions.

Cyclic voltammetry confirmed the E_g^{op} values and established the extent to which fluorine substitution lowers the LUMO energy levels of the parent hydrocarbons. Electrochemical properties are listed in Table 4, and a representative cyclic voltammogram of **7** is shown in Figure 2. Each compound exhibits one oxidation peak and one reduction peak within the potential window studied (−2.6 to +2 V, Ag/AgNO$_3$ reference electrode), except for 9,10-diphenylanthracene and the chlorinated anthracene derivatives. An irreversible second oxidation peak is seen for 9,10-diphenylanthracene at +1.45 V, which is consistent with published values.[35] As expected, extra reduction peaks are observed for the chlorinated substrates because chloride loss from the radical anion forms a neutral radical that undergoes further reactions.[36] Compared to the parent hydrocarbons, HOMO energy levels are stabilized in the fluorinated materials by 0.28−0.52 eV. More importantly, the fluorinated anthracenes have substantially lowered LUMO energy levels, with stabilizations ranging from 0.51 to 0.61 eV. Fluorine substitution on the anthracene core stabilizes LUMO energy levels more than HOMO energy levels, causing a small contraction of the electrochemical HOMO−LUMO energy gap, which corroborates the E_g^{op} data. Also listed in Table 4 are effective n-type materials and their LUMO energy levels,[7,11,37] to which the fluorinated anthracene derivatives, especially **1**, compare favorably. This electronic information indicates that 9,10-dichlorooctafluoroanthracene should be an ideal building block for extended structures with n-type behavior.

Solid-State Structure. X-ray diffraction studies were performed on crystals of **1** and **7** to determine the effect of fluorine substitution on the solid-state structure. Yellow needles of **1** were grown by vacuum sublimation at 275 °C, and some important packing features are shown in Figure 3. The parent hydrocarbon, 9,10-dichloroanthracene, has two polymorphs, with the β form (grown by sublimation) being the appropriate comparison.[39] This polymorph of the non-fluorinated analogue shows slipped π stacking with an average distance between planes of 3.5 Å and no C−C short contacts. A tilt angle of 43° exists between the anthracene planes of neighboring π stacks, and the chlorine atoms are coplanar with the rest of the molecule. In contrast, **1** demonstrates π stacking with a shorter vertical distance (3.27 Å between planes) but larger lateral slipping, giving a C−C short contact of 3.39 Å. The edge-on C−F interactions (at 3.00 and 3.03 Å) induce a much larger tilt angle of 81° between the anthracene planes of adjacent π stacks in **1**, and the chlorine atoms bend 4° out of plane on opposite faces of the ring system.

More notably, fluorine substitution on the 9,10-diphenylanthracene framework considerably improves π stacking. For

---

[34] See Supporting Information for thin-film UV−vis spectra of **1** and **7**.

[35] Perichon, J. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A., Lund, H., Eds.; Marcel Dekker: New York, 1978; Vol. XI, pp 71−161.

[36] Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Saveant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.

[37] Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

[38] Matsumoto, T.; Sato, M.; Hirayama, S. *Chem. Lett.* **1972**, 603.

[39] Burshtein, Z.; Hanson, A. W.; Ingold, C. F.; Williams, D. F. *J. Phys. Chem. Solids* **1978**, *39*, 1125.

TABLE 4. Electrochemical Properties[a]

compound	E_{ox}[b] (V)	E_{red}[b] (V)	HOMO[c] (eV)	LUMO[c] (eV)	E_g^{el} (eV)
anthracene[d]	+0.99	−2.40	−5.55	−2.43	3.12
9,10−dichloroanthracene[d]	+1.17	−1.97, −2.19[e], −2.40[e]	−5.75	−2.85	2.90
9,10−diphenylanthracene[d]	+0.94, +1.45[f]	−2.29	−5.51	−2.53	2.98
2	+1.53	−1.77	−6.07	−3.03	3.04
1	+1.45	−1.49, −1.67[e], −1.81[e]	−6.03	−3.46	2.57
7	+1.39	−1.77	−5.93	−3.04	2.89
perfluoropentacene[g]				−3.65	
C_{60}[h]				−3.91	
C_8F_{15}−NTCDI[i]				−4.00	

[a] Acetonitrile, $(Bu)_4NPF_6$ electrolyte, $Ag/AgNO_3$ reference, 200 mV/s scan rate. [b] E_{ox} and E_{red} calculated from the potential at peak current (anodic and cathodic sweeps, respectively). [c] HOMO and LUMO energy levels (relative to vacuum) calculated from the onset of oxidation and reduction, respectively. [d] Consistent with published values (see refs 35 and 38). [e] Further reductions following decomposition of the radical anion. [f] Second oxidation. [g] LUMO energy level estimated from ref 11. [h] LUMO energy level estimated from ref 37. [i] LUMO energy level estimated from ref 7.

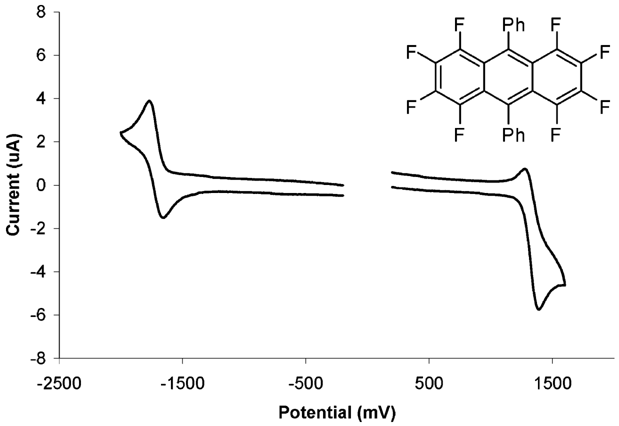


FIGURE 2. Cyclic voltammogram of **7**.

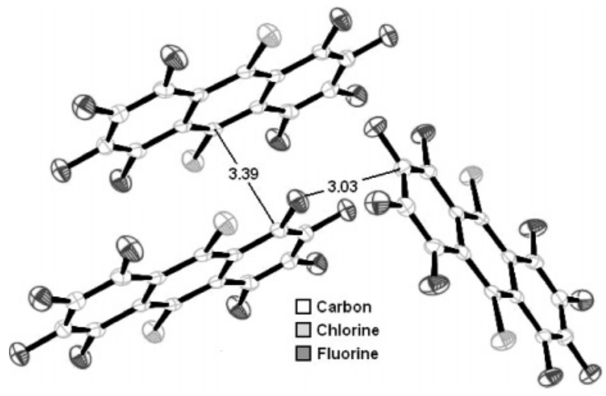


FIGURE 3. Crystal packing in **1**, all values in angstroms.

example, 9,10-diphenylanthracene packs in a herringbone pattern (66° tilt angle) along the axis of the phenyl substituents.[40] The edge-on C−H interactions dominate the intermolecular forces (no π stacking), and the phenyl groups are twisted 68° relative to the anthracene plane. Conversely, **7** π stacks in a "bricklayer" structure (C−C short contacts of 3.38 and 3.39 Å as shown in Figure 4) with a slight tilt of 6° between alternating rows of molecules. A view down the *a*-axis (Figure 5) clearly illustrates the perpendicular nature of the phenyl substituents (89°) as well as the 19° tilt between anthracene planes on neighboring π stacks. Such extensive π stacking of perfluorinated aromatic rings should lead to efficient electron transport in well-ordered thin films.

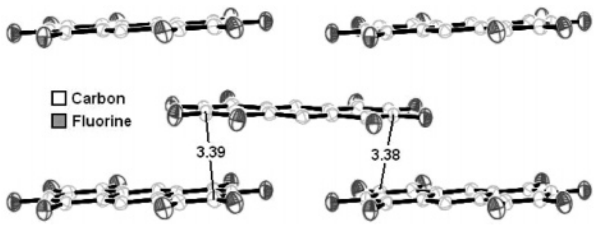


FIGURE 4. View down the *c*-axis in crystals of **7**, phenyl groups removed for clarity and all values in angstroms.

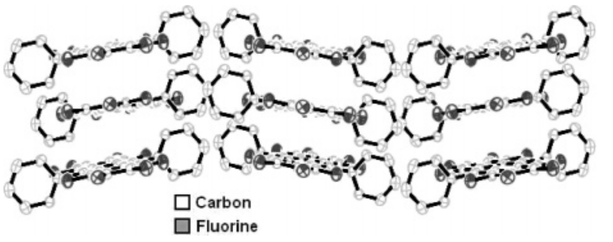


FIGURE 5. View down the *a*-axis in crystals of **7**, hydrogen atoms removed for clarity.

Conclusion

Compound **1** has been shown to be a viable building block for potential n-type organic semiconductors. Other boronic acids are currently being explored as coupling partners along with aryltin reagents (Stille coupling[41]) and terminal alkynes (Sonogashira coupling[42]). Expanding the coupling chemistry of **1** should lead to effective electron-transport materials through fine control of electronic properties and solid-state structure.

Experimental Section[43]

Tetrafluorophthalic Anhydride (3). A 500 mL three-necked flask equipped with a reflux condenser and an addition funnel was charged with tetrafluorophthalic acid (129.01 g, 0.54 mol). Thionyl chloride (168 mL, 2.30 mol) was added dropwise over 15 min at 60 °C. The subsequent white suspension was heated at 90 °C for 14 h to afford a light-brown solution. The excess thionyl chloride was removed under vacuum (20 Torr) at 60 °C, and the resulting

---

(40) Adams, J. M.; Ramdas, S. *Acta. Crystallogr., Sect. B* **1979**, *35*, 679.

(41) Mitchell, T. N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 125−161.

(42) Marsden, J. A.; Haley, M. M. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 317−394.

(43) See Supporting Information for general experimental details.

ivory solid was dried under high vacuum. Sublimation (100 °C, 0.2 Torr) gave a colorless crystalline solid (115.36 g, 97%): mp 93−94 °C (lit.[14] 94−95.5 °C).

Dilactone 9. A 500 mL flask equipped with a reflux condenser was charged with **3** (10.00 g, 45.44 mmol) and *m*-xylene (50 mL). The solution was heated to 160 °C, anhydrous cesium fluoride (10.00 g, 65.83 mmol) was added, and the suspension was stirred for 24 h. Another portion of cesium fluoride (10.00 g, 65.83 mmol) was added, and the reaction was stirred for a further 24 h. The organic products were extracted into hot toluene (150 mL) and were washed with water (150 mL). Concentration of the toluene layer afforded an ivory solid that was purified by sublimation (120 °C, 0.005 Torr). Recrystallization from ethanol gave 3.60 g (40%) of colorless needles: mp 176−177 °C (lit.[16] 177−178 °C). Single crystals for X-ray diffraction were obtained by slow evaporation of a chloroform-*d*/dichloromethane solution. ^{19}F NMR: δ −133.82 (m, 2 F), −139.28 (m, 2F), −141.39 (m, 2F), −144.37 (m, 2F). GC−MS (EI) *m/z*: 396 (M^+). Anal. Calcd for $C_{15}F_8O_4$: C, 45.48; H, 0.00. Found: C, 45.12; H, <0.2.

1,2,3,4,5,6,7,8-Octafluoroanthraquinone (4). A 500 mL flask equipped with a reflux condenser was charged with **3** (5.00 g, 22.72 mmol) and *m*-xylene (50 mL). The solution was heated to °160 C, and anhydrous cesium fluoride (5.00 g, 32.92 mmol) was added. The resulting suspension was stirred for 30 min followed by dropwise addition (over 5 min) of preheated (60 °C) sulfolane (30 mL). When gas generation ceased (30 min) the red-brown mixture was cooled to 120 °C and *m*-xylene was removed under vacuum (20 Torr). Subsequent vacuum removal of sulfolane (160 °C, 0.5 Torr) left a dark-brown residue that was suspended in water/methanol (4:1, 50 mL) and was stirred at ambient temperature for 1 h. A light-brown solid was collected by filtration. The product was washed successively with water and water/methanol (1:1) and was dried under vacuum at 50 °C. The solid contained a 1:0.22 molar ratio of **4** and **10**. Sublimation (220 °C, 0.005 Torr) over 14 h gave 2.52 g of a light-yellow solid that contained **4** and a trace amount of **10**, while the sublimation residue mainly contained **10**. The crude **4** was recrystallized from benzene to afford 2.34 g (59%) of pale yellow needles: mp (DSC) 346−347 °C (lit.[16] 342−343 °C). ^{19}F NMR: δ −137.39 (m, 4F), −143.34 (m, 4F).

Lactone 10. The combined sublimation residues from several optimization reactions were purified by column chromatography (silica gel, cyclohexane/THF = 20:1 to 5:1). Recrystallization from toluene gave colorless fine needles: mp 294−296 °C. ^{19}F NMR: δ −135.96 (m, 1 F), −136.85 (m, 2F), −138.31 (m, 2F), −140.76 (m, 1F), −143.31 (m, 2F), −144.17 (m, 1F), −146.95 (m, 1F), −148.60 (m, 2F). MS (EI) *m/z*: 528 (M^+). Anal. Calcd for $C_{21}F_{12}O_3$: C, 47.75; H, 0.00. Found: C, 47.98; H, <0.2.

9,9,10,10-Tetrachlorooctafluoro-9,10-dihydroanthracene (5). A 100 mL flask was charged with **4** (8.29 g, 23.54 mmol) and phosphorus pentachloride (17.60 g, 84.52 mmol). Phenylphosphonic dichloride (32 mL, 0.23 mol) was added, and the reaction was initially heated to 130 °C for 2 h followed by stirring at 170 °C for 24 h. The resulting orange solution was diluted with toluene (200 mL) and was washed successively with water (2 × 200 mL), aq $NaHCO_3$ (saturated, 2 × 100 mL), and brine (100 mL). The organic layer was then concentrated in vacuo to a yellow oil. Methanol (200 mL) was added and the precipitate was collected by vacuum filtration to give 9.00 g (83%) of white powder: mp 239−240 °C (patent lit. 243 °C[19]). ^{19}F NMR: δ −128.61 (m, 4F), −150.11 (m, 4F). MS (EI) *m/z*: 460 (M^+). Anal. Calcd for $C_{14}Cl_4F_8$: C, 36.40; H, 0.00. Found: C, 36.27; H, <0.2.

9,10-Dichlorooctafluoroanthracene (1). A 500 mL flask equipped with a reflux condenser was charged in air with **5** (8.50 g, 18.40 mmol), NMP (150 mL), and glacial AcOH (50 mL). The solution was stirred under nitrogen at 115 °C for 24 h, and the resulting dark-brown mixture was cooled to ambient temperature. The organic products were extracted with chloroform (150 mL) and were washed with water (2 × 150 mL), aq $NaHCO_3$ (saturated, 2 × 150 mL), and brine (150 mL). Concentration of the organic layer afforded a brown oil that was precipitated from methanol (200 mL). The crude solid was then dissolved in chloroform and was passed through a plug of silica gel (hexanes eluant) to give 6.12 g (85%) of bright yellow powder: mp 172−173 °C (patent lit. 172 °C[28]). Single crystals for X-ray diffraction were obtained by sublimation (275 °C) under static vacuum (0.02 Torr). ^{19}F NMR: δ −137.09 (d, J = 12 Hz, 4F), −152.35 (d, J = 12 Hz, 4F). GC−MS (EI) *m/z*: 390 (M^+). Anal. Calcd for $C_{14}Cl_2F_8$: C, 43.00; H, 0.00. Found: C, 43.02; H, <0.2.

9-Chloro-1,2,3,4,5,6,7,8-octafluoroanthracene (11). The combined mixtures from several aromatization reactions were purified by column chromatography (silica gel, hexanes). Recrystallization from ethanol gave yellow needles that were contaminated with 4 mol % of **2**. ^{1}H NMR: δ 8.80 (s, 1 H). ^{19}F NMR: δ −139.95 (m, 2F), −148.51 (m, 2F), −153.52 (m, 2F), −155.31 (m, 2F). GC−MS (EI) *m/z*: 356 (M^+). Anal. Calcd for $C_{14}HClF_8$ + 4 mol % of $C_{14}H_2F_8$: C, 47.34; H, 0.29. Found: C, 47.37; H, 0.10.

1,2,3,4,5,6,7,8-Octafluoro-9,10-dihydroanthracene (6). A 50 mL flask equipped with a reflux condenser was charged in air with **5** (0.54 g, 1.17 mmol), zinc dust (1.00 g, 15.29 mmol), NMP (9 mL), and glacial AcOH (3 mL). The suspension was stirred under nitrogen at 110 °C for 16 h followed by cooling to ambient temperature. The organic products were extracted with ether (25 mL) and were washed with water (2 × 25 mL), aq $NaHCO_3$ (saturated, 2 × 25 mL), and brine (25 mL). Concentration of the organic layer gave a tan solid that was rinsed with methanol (3 × 10 mL) to afford 0.35 g (92%) of white powder: mp 145−147 °C. ^{1}H NMR: δ 4.00 (s, 4H). ^{19}F NMR: δ −144.64 (m, 4F), −159.65 (m, 4F). MS (EI) *m/z:* 324 (M^+). Anal. Calcd for $C_{14}H_4F_8$: C, 51.87; H, 1.24. Found: C, 51.54; H, 1.15.

1,2,3,4,5,6,7,8-Octafluoroanthracene (2). A 250 mL flask equipped with reflux condenser was charged in air with **4** (1.00 g, 2.84 mmol), zinc dust (4.00 g, 61.17 mmol), and glacial AcOH (50 mL). The reaction mixture was stirred under nitrogen at 120 °C for 4 days followed by cooling to ambient temperature. The organic products were extracted with ether (50 mL) and were washed with water (2 × 50 mL), aq $NaHCO_3$ (saturated, 2 × 50 mL), and brine (50 mL). Concentration of the organic layer left crude **6**, which was added to a 250 mL flask containing activated carbon (1.00 g) and toluene (50 mL). The suspension was stirred under reflux for 4 days in air and was then filtered to afford a faint yellow solution. The removal of solvent in vacuo and subsequent recrystallization from ethanol gave 0.75 g (82%) of colorless needles: mp 175 °C. ^{1}H NMR: δ 8.86 (s, 2H). ^{19}F NMR: δ −150.14 (d, J = 15 Hz, 4F), −156.65 (d, J = 15 Hz, 4F). GC−MS (EI) *m/z:* 322 (M^+). Anal. Calcd for $C_{14}H_2F_8$: C, 52.20; H, 0.63. Found: C, 52.27; H, 0.45.

1,2,3,4,5,6,7,8-Octafluoro-9,10-diphenylanthracene (7). Phosphine **8** (0.03 g, 0.06 mmol), tris(dibenzylideneacetone)dipalladium-(0) (0.01 g, 0.01 mmol), sodium carbonate (0.21 g, 2.00 mmol), phenylboronic acid (0.24 g, 2.00 mmol), and **1** (0.30 g, 0.77 mmol) were loaded into a 25 mL 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 15 h. The organic products were extracted with dichloromethane (25 mL) and were washed with aq $NaHCO_3$ (saturated, 3 × 25 mL). The organic layer was passed through a plug of silica gel (hexanes eluant) and was then concentrated to afford a pale yellow solid. Slow cooling of a toluene solution gave 0.30 g (82%) of yellow crystals: mp (DSC) 328 °C. ^{1}H NMR: δ 7.46−7.55 (m, 6H), 7.38−7.42 (m, 4H). ^{19}F NMR: δ −134.94 (d, J = 13 Hz, 4F), −156.08 (d, J = 13 Hz, 4F). GC−MS (EI) *m/z:* 474 (M^+). Anal. Calcd for $C_{26}H_{10}F_8$: C, 65.83; H, 2.12. Found: C, 66.06; H, 2.10.

Acknowledgment. This work was supported by the National Science Foundation research grant CHE0314709. The authors thank Professor David Milstein for helpful discussions on C−C coupling chemistry and Dr. Barry Thompson for advice on UV−vis/fluorescence spectroscopy and cyclic voltammetry.

Supporting Information Available: General experimental details, UV−vis/fluorescence spectra of **1** and **2**, thin-film UV−vis spectra of **1** and **7**, cyclic voltammograms of **1** and **2**, ^{1}H and ^{19}F NMR spectra of **11**, and crystallographic data (CIF) for **1**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070404A