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Pinpoint-Fluorinated Phenacenes: New Synthesis and Solubility Enhancement Strategies

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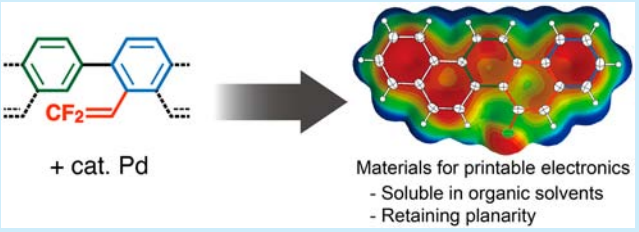
Supporting Information

ABSTRACT: The Pd(II)-catalyzed cyclizations of 2,2-difluorovinylated biaryls, following a Friedel−Crafts-type mechanism, provide a new route to pinpoint-fluorinated phenacenes. The single fluorine substituent stabilized the synthesized fluoropicenes (fluoro[5]phenacenes) toward aerial oxidation and contributed to their solubility in organic solvents. For example, 6- and 13-fluoropicenes were 25- and 15-fold more soluble in THF than nonfluorinated picene. X-ray crystal structure analysis revealed that the fluorine substituent did not alter molecular planarity.



Phenacenes are a subclass of polycyclic aromatic hydrocarbons (PAHs) that are comprised of ortho-fused benzene rings in a zigzag configuration. Linear acenes are established organic semiconducting materials[1,2] but display air and light sensitivity.[3] Conversely, phenacenes, which exhibit higher stability than acenes because of their low-lying highest occupied molecular orbitals, have emerged as important alternatives for these materials.[4]

Our continuing studies on reactions involving fluorinated alkenes[5,6] and allenes[7] have prompted our interest in regioselectively *monofluorinated* phenacenes. These pinpoint-fluorinated phenacenes are expected to serve as organic semiconducting materials.[8] Among important factors in developing organic semiconducting materials (e.g., carrier mobility, on/off ratio, etc.), we have focused our attention particularly on solubility of pinpoint-fluorinated phenacenes.

The introduction of a single fluorine substituent into phenacene skeletons presents several advantages as follows:[8,9]

(i) The fluorine substituent displays high electronegativity, which decreases the electron density of phenacene π systems and, therefore, enhances their resistance to aerial oxidation.

(ii) The fluorine substituent has lone pairs in its 2p orbitals. These lone pairs present repulsive interaction with adjacent π-electrons in the 2p orbitals, perturbing the electron density of the π-systems.

(iii) The fluorine substituent displays a low steric impact. Therefore, its introduction into phenacene molecules should not change their shape.

The effects of the electronegativity (i) and fluorine lone pairs (ii) induce polarization in molecules.[10] We hypothesized that the polarization might contribute to enhanced solubility of pinpoint-fluorinated phenacenes in polar organic solvents, which is required in wet processes of device fabrication.[11] The small steric effect (iii) would result in the preservation of planarity in the π-system, which is necessary for inducing self-assembly of the molecules.[2b] In addition, other effects of the fluorine substituent such as the restriction of intermolecular C−H/π interactions could also lead to solubility enhancement.

In spite of these promising features, few studies have focused on the properties and structures of pinpoint-fluorinated phenacenes, presumably because of their difficult synthesis. Various methods have been developed to produce non-fluorinated phenacenes. The photochemical oxidative cyclization of stilbene derivatives, originally established by Mallory,[12] has given the longest [11]phenacenes.[13] Diels−Alder reactions,[14] Friedel−Crafts-type ring closures,[15] Ru- or Pt-catalyzed cyclizations of alkynyl biaryls,[16] and other metal-catalyzed reactions[17] have also been addressed. However, the fluorination of the aromatic nuclei is the only way to synthesize pinpoint-fluorinated phenacenes.[18] This approach has resulted in a regioselective monofluorination of higher-order phenacene skeletons, albeit with difficulty. Herein we present strategies to synthesize pinpoint-fluorinated phenacenes and to solve the solubility problem of the parent phenacenes.

The electrophilic activation of 1,1-difluoro-1-alkenes was achieved by a cationic palladium(II) catalyst.[5] When treated with a catalytic amount of $[Pd(MeCN)_4](BF_4)_2$ in the presence of $BF_3{\cdot}OEt_2$ in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP),[19] 1,1-difluoroalkenes bearing a 2-arylethyl group provided α-tetralones upon spontaneous hydrolysis of the formed cyclic vinyl fluorides.[5a] In this reaction, π-coordination with Pd(II) promoted a selective Friedel−Crafts-type cyclization at the vinylic CF_2 carbon. Using this concept, we devised a new strategy for the synthesis of pinpoint-fluorinated phenacenes. Specifically, the 2-arylethyl moiety was replaced with a biaryl moiety in the substrates to provide target fluorophenacenes,

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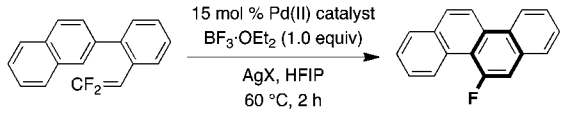
which should be hydrolytically stable because of their aromaticity.

2,2-Difluorovinylated biaryls such as **1a** were readily prepared (i) by a Wittig-type difluoromethylenation of biaryl carbaldehydes (C1 introduction)[20] or (ii) by a palladium-catalyzed difluorovinylation of biaryl triflates or halides (C2 introduction)[21] (see the Supporting Information). Screening of catalysts for the cyclization of **1a** revealed that in situ generated palladium(II) catalysts exhibit higher catalytic activities (Table 1). In the presence of $[Pd(MeCN)_4](BF_4)_2$, substrate **1a** gave

Table 1. Catalyst Effects on Chrysene Synthesis



1a **2a**, single regioisomer

entry	Pd(II) catalyst	**2a**[a] (%)	recovery of **1a**[a] (%)
1	$[Pd(MeCN)_4](BF_4)_2$	15	63
2	$Pd(MeCN)_2Cl_2$, AgOTf (1:2)	24	54
3	$PdCl_2$, AgOTf (1:2)	81	2
4	$PdCl_2$, AgOTf (1:1)	68	22
5	$PdCl_2$	7	93
6	$PdCl_2$, $AgBF_4$ (1:2)	78	24
7	$PdCl_2$, $AgSbF_6$ (1:2)	63	33

[a] ^{19}F NMR yield based on $PhCF_3$ as an internal standard.

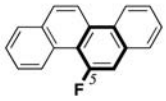
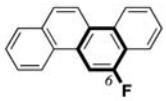
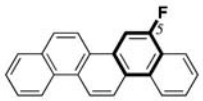
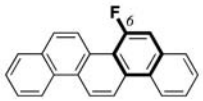
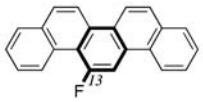
the corresponding 5-fluorochrysene ([4]phenacene, **2a**) as a single regioisomer only in 15% yield (60 °C, 2 h, entry 1).[5a] The regiochemistry in the cyclization of **1a** stems from the high reactivity of the naphthalene α carbon toward electrophilic aromatic substitution. The cationic palladium(II) species generated from $Pd(MeCN)_2Cl_2$ and silver trifluoromethanesulfonate (AgOTf) afforded **2a** in 24% yield (entry 2). Acetonitrile ligand removal from the starting catalyst dramatically improved the yield of **2a** to 81% (entry 3). The use of two equiv of AgOTf to $PdCl_2$ gave the best yield of **2a** (entries 3–5).[22,23] Silver tetrafluoroborate ($AgBF_4$) and hexafluoroantimonate ($AgSbF_6$) provided somewhat less promising results (entries 6 and 7).

The ligand-free palladium(II) catalyst achieved a regioselective synthesis of pinpoint-fluorinated [4]- and [5]-phenacenes (Table 2). Single isomers of 5- (**2a**) and 6-fluorochrysenes (**2b**) were obtained in 81% and 77% yields, respectively, starting from the corresponding difluorovinylated biaryls (entries 1 and 2). Synthesis of 5- (**2c**), 6- (**2d**), and 13-fluoropicenes (**2e**) was also accomplished under similar conditions in 47%, 70%, and 85% yields, respectively (entries 3–5). These fluorinated chrysenes and picenes were stable enough to conduct chromatographic purifications without requiring any specific precaution.

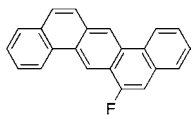
A mechanism for the phenacene synthesis is proposed in Figure 1. Substrates **1** coordinate to the cationic palladium(II) center to form π complexes **A**, in which the electron density of the difluoroalkene moiety is lowered, leading to its electrophilic activation. This promotes a Friedel–Crafts-type ring closure, providing cyclic alkylpalladium intermediates **B** that in turn undergo a BF_3-assisted β-fluorine elimination to yield product **2**. The formation of BF_4^- regenerates the active cationic palladium(II) species in this process.

The charge distributions of the parent nonfluorinated and the synthesized 5- (**2c**), 6- (**2d**), and 13-fluoropicenes (**2e**)

Table 2. Synthesis of Pinpoint-Fluorinated Chrysenes and Picenes[a]

entry	t (h)	F–PAH		**2**[b] (%)
1	2		**2a**	75, 81 [c,d]
2	3		**2b**	51,[c] 77 [d]
3	3		**2c**	47[f]
4	4		**2d**	70 (90:10) [g]
5	1		**2e**	85 [e]

[a] Conditions: **1**, 15 mol % $PdCl_2$, 30 mol % AgOTf, BF_3·OEt_2 (1.0 equiv), HFIP, 60 °C. [b] Isolated yield unless otherwise noted. [c] Single regioisomer. [d] ^{19}F NMR yield based on $PhCF_3$ as an internal standard. [e] The decrease in the isolated yield results from the difficult chromatographic separation. [f] 25 mol % $PdCl_2$, 50 mol % AgOTf, BF_3·OEt_2 (1.0 equiv). [g] Regioisomeric ratio (**2d**:**3**) determined by ^{19}F NMR spectroscopy.



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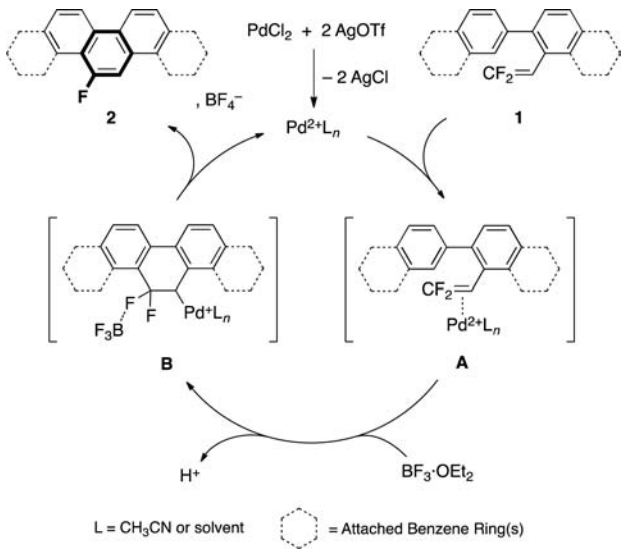

Figure 1. Proposed catalytic cycle for fluorophenacene synthesis.

were analyzed by density functional theory (DFT) calculations. As expected, the introduction of a single fluorine substituent into the picene skeleton greatly perturbed the electron density of the π-systems and effectively induced polarization (Figure 2). The parent picene exhibited symmetrical and even contours in

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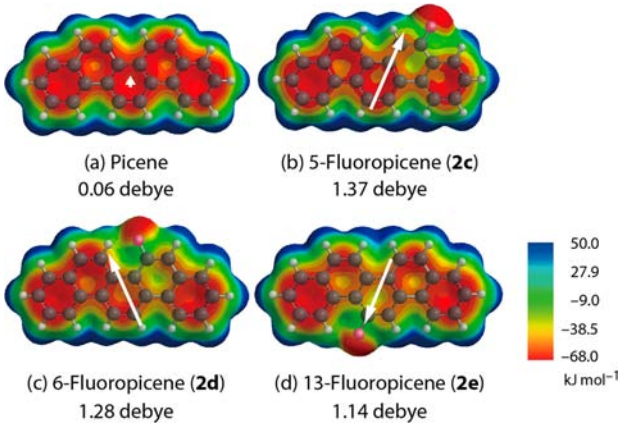

Figure 2. DFT electrostatic potential maps and dipole moments of pinpoint-fluorinated phenacenes (B3LYP/6-31G* level). White arrows represent dipole moments for each picene.

the electrostatic potential map (a). In contrast, the potential maps of the pinpoint-fluorinated picenes were not symmetrical (b–d). Fluorinated picenes thus showed a higher degree of desymmetrization in their charge distribution and their dipole moments rose from 0.06 D (parent picene) to 1.14–1.37 D.

These pinpoint-fluorinated PAHs displayed high solubility in organic solvents (Table 3). A saturated THF solution presented a low concentration of parent picene (6.4×10^{-3} mol L^{-1}) at room temperature, based on its molar extinction coefficient ε determined by UV–vis spectroscopy. On the other hand, the measured solubilities amounted to 1.4×10^{-2}, 1.6×10^{-1}, and 9.3×10^{-2} mol L^{-1} for **2c**, **2d**, and **2e**, respectively. These values correspond to 2-, 25-, and 15-fold that of the parent picene.

Table 3. Solubility of Pinpoint-Fluorinated Picenes in THF

		concentration (mol L^{-1})	
entry	phenacene	mol L^{-1}[a]	wt %
1	picene	6.4×10^{-3} (1)	0.20
2	5-fluoropicene (**2c**)	1.4×10^{-2} (2)	0.48
3	6-fluoropicene (**2d**)	1.6×10^{-1} (25)	5.3
4	13-fluoropicene (**2e**)	9.3×10^{-2} (15)	3.1

[a]Solubility relative to that of the parent picene is shown in parentheses.

Organic substituents such as *tert*-butyl or phenyl groups are often employed to increase the solubility of polycyclic aromatic compounds. However, these bulky substituents affect molecular planarity. For example, the previously reported soluble [7]phenacene derivative bearing *tert*-butyl groups was enormously twisted.[24] In contrast, X-ray crystal structure analysis revealed that the π-systems of the synthesized **2d** and **2e** remained planar (Figure 3). Therefore, the fluorine substituent introduced into the phenacene skeleton did not change the shape of these molecules because of its small steric requirement. Planarity of aromatic compounds is an important factor that induces self-assembly of their benzene rings into π-stacked arrays, which leads to high performance as organic semiconducting materials.[2b,c] Thus, introduction of a single fluorine substituent is a suitable strategy for enhancing phenacene solubility without affecting their performance as materials for electronic devices. Fluoropicene **2e** actually exhibits p-type semiconducting behavior (see the Supporting Information).[25]

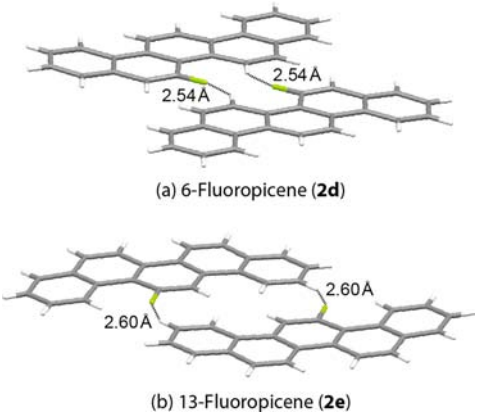

Figure 3. X-ray crystal structures of (a) 6-fluoropicene (**2d**) and (b) 13-fluoropicene (**2e**).

The X-ray crystal structure analysis showed that two molecules of pinpoint-fluorinated picenes were coupled through C–H···F interactions in solid state (2.54 and 2.60 Å for H···F distances in **2d** and **2e**, respectively, and 2.67 Å for the sum of the van der Waals radii of hydrogen and fluorine, Figure 3)[26] and that the dimer formed face-to-face stacks (see the Supporting Information). The fluorine substituent thus decreased C–H/π interactions, which usually organize aromatic molecules in solid state, and might contribute to the solubility enhancement.

It should be mentioned that some groups[27] have recently reported that packing structures of acene derivatives were controlled by introducing a polyfluorinated aromatic moiety to their frameworks through the use of C–H···F and Ar–FAr interactions. However, the compound was hardly soluble in organic solvents because of the packing structure stabilized by the tight interactions.[27c] Again, introduction of a single fluorine substituent to PAHs is a suitable strategy for development of solution-processable organic semiconducting materials.

In summary, the Pd(II)-catalyzed cyclization of 2,2-difluorovinylated biaryls was studied to synthesize pinpoint-fluorinated phenacenes, which are stable toward aerial oxidation and soluble in THF. Our synthetic and solubility enhancement strategies by introducing one fluorine substituent provide promising materials that are suitable for printable organic electronics.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectra of new compounds, a summary of the patent document,[25] photophysical properties obtained by UV–vis spectroscopy, and packing structures of **2d** and **2e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(22) As suggested by the poor result in entry 5, $BF_3{\cdot}OEt_2$ alone failed to promote the reaction, and a cationic palladium catalyst was required.
(23) The attached benzo moiety of difluoroalkene **1a** might readily coordinate to the palladium(II) center and deactivate the catalyst in the chrysene synthesis. The ligand-free palladium(II) species, generated in situ from $PdCl_2$ and AgOTf, is more active than ligated complex $[Pd(MeCN)_4](BF_4)_2$ and may produce better results.
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