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Pinpoint-fluorinated polycyclic aromatic hydrocarbons (F-PAHs): Syntheses of difluorinated subfamily and their properties

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ARTICLE INFO

Dedicated to Professor Antonio Togni with recognition on the occasion of his being awarded the 2017 ACS Award for Creative Work in Fluorine Chemistry.

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ABSTRACT

Difluorinated polycyclic aromatic hydrocarbons (PAHs) containing three to five benzene rings were systematically synthesized by the Pd(II)-catalyzed Friedel–Crafts-type cyclization of 1,1,2-trifluoro- and 1,1-difluoro-1-alkenes and the In(III)-catalyzed tandem cyclization of bis(1,1-difluoroallene)s. Using an array of the difluorinated PAHs that were obtained and previously reported monofluorinated PAHs, the physical properties of the pinpoint-fluorinated PAHs were investigated. (i) The ^{19}F NMR signals of the bay-region fluorine atoms were shifted downfield by ca. 8–14 ppm for *vic*-difluorinated PAHs and ca. 11–19 ppm for non-*vic*-difluorinated and monofluorinated PAHs. (ii) The introduction of fluorine into PAH molecules increased their solubilities in organic solvents, which was best exemplified by the high solubilities of 6,7-difluoropicene (5.4 wt%) and 6-fluoropicene (5.3 wt%) in THF. (iii) The HOMO–LUMO energy gaps of the pinpoint-fluorinated PAHs were smaller than that of the corresponding fluorine-free PAH (*i.e.*, picene) by 0.02–0.26 eV, and the HOMO and LUMO energy levels were lowered by 0.10–0.22 eV and 0.12–0.41 eV, respectively.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds that comprise *ortho-* and/or *peri*-fused benzene rings in various configurations [1]. Acenes and phenacenes are representatives of this class of molecules with a linear and zigzag configuration, respectively. Importance of these PAHs as organic semiconducting materials is increasing significantly in the field of materials science [2]. Therefore, the development of methods for the synthesis of PAHs is becoming an important issue.

Regioselectively mono- or difluorinated (pinpoint-fluorinated) PAHs (F-PAHs, Fig. 1) are a promising class of organic semiconducting materials because of the unique properties of the fluorine substituent(s) (Fig. 2) [3]: (a) The high electronegativity of fluorine leads to an increase in the resistance of the fluorinated PAHs to aerial oxidation by lowering the energy levels of their HOMO. (b) The repulsive interaction between the lone pairs in the fluorine 2p orbitals and the adjacent π-electrons in the carbon 2p orbitals perturbs the electron distribution in the extended π-system [4]. The induced polarization renders PAHs highly soluble in polar solvents, leading to printable organic electronic devices [5]. (c) From the viewpoint of steric bulk, the low steric demand of fluorine, the introduction of which into PAHs causes no significant change in their molecular shape, would have little effect on their π-π stacking in the solid state. Thus, the electronic and steric effects of attaching single or double fluorine substituent(s) to PAH skeletons can endow them with advantageous semiconducting properties, as exemplified by fluorinated picenes, which are soluble in THF and exhibit p-type semiconducting behavior [6,7].

In spite of their potential, however, studies of pinpoint-fluorinated PAHs have been hampered by the lack of available methods for their systematic synthesis [8]. Synthetic approaches to fluorinated aromatic compounds are broadly classified into two categories: (i) strategies for the introduction of fluorine (Scheme 1) and (ii) strategies for the construction of fluorinated rings. Although the regioselective introduction of fluorine into aromatic systems has been studied for a long time [9], it has drawbacks, namely, the need for the prior regioselective introduction of a functional group (a) or a directing group (b) to control the regioselectivity of the reaction, as well as the construction of the PAH skeleton. In spite of its efficiency, the construction of fluorinated aromatic rings has been limited to the oxidative photocyclization or the coupling reaction of *cis*-stilbene derivatives [10].

By means of the latter strategy, we have reported the synthesis of pinpoint-fluorinated phenacenes by the cyclization of 1,1-difluoro-1-alkenes catalyzed by cationic Pd(II) species (Fig. 3) [6]. 1,1-

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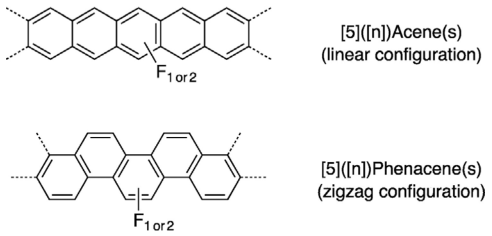


Fig. 1. Structures of pinpoint-fluorinated acenes and phenacenes (n refers to the number of benzene rings).

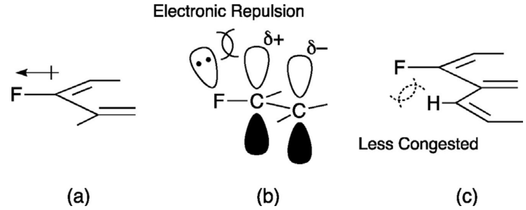
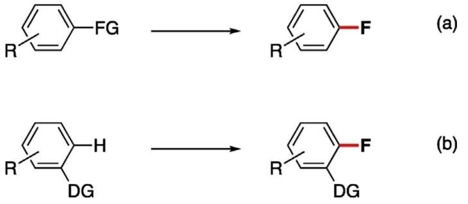


Fig. 2. Electronic and steric effects of a fluorine substituent on an adjacent π system.



Scheme 1. Strategies for the introduction of fluorine to form fluoroarenes (FG = functional group; DG = directing group).

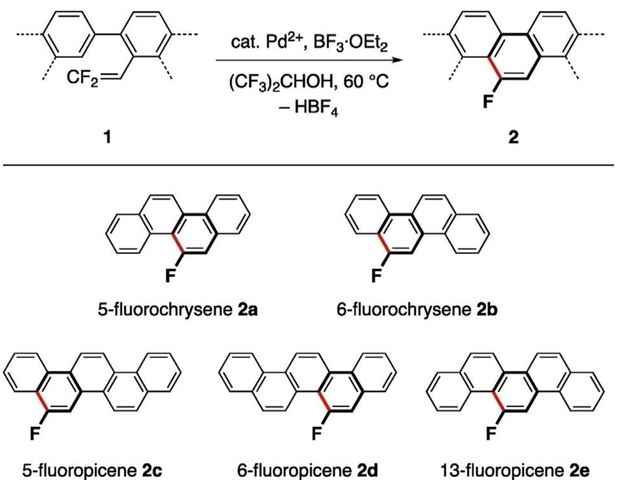


Fig. 3. Strategy for the construction of fluorinated rings to form fluoroarenes: electrophilic activation of 1,1-difluoro-1-alkenes (synthesis of pinpoint-monofluorinated phenacenes).

Difluoroalkenes **1**, possessing an *o*-biphenyl skeleton were treated with a catalytic amount of $[\mathrm{Pd(MeCN)_4}](\mathrm{BF_4})_2$ or $\mathrm{PdCl_2}$/AgOTf (1:2) in the presence of boron trifluoride etherate (1.0 equiv) in 1,1,1,3,3,3-hexafluoropropan-2-ol [11]. Pinpoint-monofluorinated chrysenes ([4]phenacenes) **2a** and **2b** and picenes ([5]phenacenes) **2c–e** were synthesized in good yields, although *difluorinated* PAHs have not yet been synthesized by this protocol.

In this paper, the syntheses of pinpoint-difluorinated PAHs involving the Pd(II)-catalyzed Friedel–Crafts-type cyclization of 1,1,2-trifluoro- and 1,1-difluoro-1-alkenes and the In(III)-catalyzed Friedel–Crafts-type cyclization of 1,1-difluoroallenes are described. The assembly of an array of difluorinated PAHs formed via these protocols and previously reported monofluorinated PAHs, which mainly comprised phenacenes, enabled studies of their physical properties such as solubility, downfield shift in ^{19}F NMR spectroscopy, and HOMO/LUMO energy gap.

2. Results and discussion

2.1. Synthesis of vic-difluorinated PAHs

Although *vic*-difluorinated aromatic compounds constitute an attractive subfamily of pinpoint-fluorinated PAHs, their selective synthesis has been rare [12]. We envisioned that the employment of 1,1,2-trifluoro-1-alkenes as substrates for the aforementioned electrophilic cyclization (Friedel–Crafts-type cyclization) would enable the facile construction of *vic*-difluorinated PAHs.

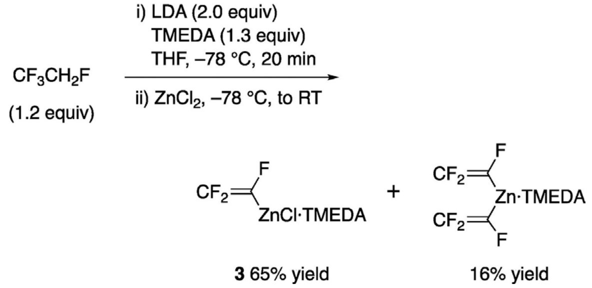
2.1.1. Preparation of 1,1,2-trifluoro-1-alkenes

The required 1,1,2-trifluoro-1-alkenes were prepared by the Negishi coupling of a trifluorovinylzinc(II) complex with the corresponding aryl triflates or iodides [13]: Trifluorovinyllithium, which was generated from commercially available 1,1,1,2-tetrafluoroethane and LDA (2.0 equiv), was treated with zinc dichloride in the presence of TMEDA at −78 °C (Scheme 2). ^{19}F NMR analysis indicated that trifluorovinylzinc (II) chloride–TMEDA complex **3** (65% yield based on $\mathrm{ZnCl_2}$) was obtained along with an inseparable bis(trifluorovinyl)zinc complex (16% yield).

The Negishi coupling of trifluorovinylzinc(II) complex **3** afforded the required 1,1,2-trifluoro-1-alkenes (Table 1). Trifluoroalkene **5a**, which bears a biphenyl moiety, was prepared from **3** and commercially available 2-iodo-1,1′-biphenyl in 98% yield (Entry 1). Aryl triflates **4b** and **4c** afforded the corresponding products **5b** and **5c** in 94% and 68% yields, respectively, using a 1,3-bis(diphenylphosphino)propane (dppp) ligand (Entries 2–5). The coupling of triflates **4d** and **4e** proceeded smoothly to afford **5d** and **5e** in 27% and 85% yields, respectively (Entries 6 and 7).

2.1.2. Electrophilic cyclization of 1,1,2-trifluoro-1-alkenes

Having synthesized the required trifluoroalkenes, the Pd(II)-catalyzed electrophilic cyclization was examined (Table 2). The cyclization of trifluoroalkene **5a** proceeded under catalysis by $\mathrm{PdCl_2}$/AgOTf [6a] to afford 9,10-difluorophenanthrene (**6a**) in 47% yield (Entry 1). Cyclization on the naphthalene moiety in **5b** proceeded to afford the product as a single isomer (51% yield, Entry 2). A ^{19}F NMR study of the obtained product suggested that 5,6-difluorochrysene (**6b**) was obtained (*vide infra*). Thus, the cyclization reaction took place at the α-position of the naphthalene substructure, and the same regioselectivity was observed as in the cyclization of 1,1-difluoro-1-alkenes [6a]. The $\mathrm{PdCl_2}$/$\mathrm{AgNTf_2}$ catalytic system was effective for increasing the yield of **6**. *vic*-Difluorinated chrysene **6b** and picenes **6c/6c'** were synthesized from trifluoroalkenes **5b** and **5c** in 78% and 63% yields, respectively (Entries 3–5). As shown in Entry 6, it was revealed that cyclization on a benzene moiety was slower than on a naphthalene moiety. Phenylated trifluoroalkene **5d** afforded 5,6-difluorochrysene (**6b**) albeit only in 18%



Scheme 2. Preparation of trifluorovinylzinc(II) complex **3**.