

One-pot synthesis of partially fluorinated naphthalene, anthracene, and chrysene derivatives

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Abstract

A series of partially fluorinated naphthalene, anthracene, and chrysene derivatives have been synthesized by a convenient one-pot reaction of multi-fluorinated aromatics and 1,4-dilithio-1,2,3,4-tetraaryl-1,3-butadiene that was generated in situ from the reduction of diphenylacetylene derivatives with lithium naphthalenide.

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Polycyclic aromatic acenes (PAH) have received considerable interest in the past few decades due to their potential application for the construction of organic electronic devices.¹ Tuning of molecular properties, such as solubility, stability, and charge mobility by functionalization is the most active aspect in current synthetic research for PAH. Especially, there has been increasing interest in the incorporation of fluorine into acenes, which may contribute to tuning the electronic properties, and altering π -stacking in the solid state by exploiting aryl–fluoroaryl interactions.^{2–8}

Recently, Watson and Piers independently reported the synthesis of partially fluorinated polycyclic aromatic compounds by lithium–bromine exchange of 2,2'-dibromobiaryls and nucleophilic substitutions of aromatic fluorines.^{2,3} Anthony reported the synthesis of partially fluorinated pentacenes via quinone routes.⁴ Xi prepared the partially fluorinated naphthalene derivatives from the reaction of 1,4-dilithio-1,3-dienes and hexafluorobenzene.⁵ Swager and co-workers also reported the synthesis of a series of fluorine-containing tetracene derivatives with *N*-methyl-1,2,3,4-tetrafluoroisindole as a synthetic building block.⁶

Very recently, Tilley's group published their efforts on developing an n-type organic semiconductor by using 9,10-dichlorooctafluoroanthracene as a viable building block.⁷

Here, we present the results of our initial studies aimed at establishing a new one-pot synthetic protocol to synthesize partially fluorinated acenes. This method allowed us to synthesize a series of partially fluorinated naphthalene, anthracene, and chrysene derivatives.

The preparation of 1,4-dilithio-1,2,3,4-tetraaryl-1,3-butadiene **2** from the reaction of diphenylacetylene derivatives with metal lithium has been well studied,⁹ and now is commonly used in the synthesis of silole derivatives.¹⁰ Our continuing interest in the construction of ladder-type π -conjugated molecules by the reductive cyclization of acetylene derivatives¹¹ led us to investigate the reduction of diphenylacetylene with lithium naphthalenide (LiNaph) and to expand this reaction in the synthesis of other ladder molecules.

We found that by the treatment of **1a** (R = H) with 1 equiv of LiNaph at room temperature, 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene **2a** was produced in moderate to good yield within 5 min, which was indicated by the formation of 1,2,3,4-tetraphenyl-1,3-butadiene when the reaction mixture was quenched with water. In this reaction,

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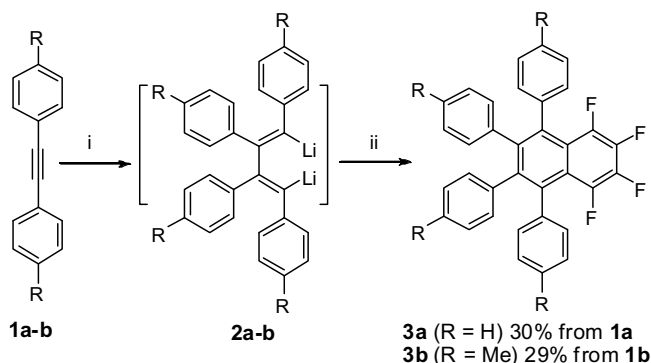
E-mail address: caihong@iccas.ac.cn (C. Xu).

the use of 1 equiv of LiNaph was crucial. When 2 equiv or more of LiNaph was used, 1,2-dilithio-1,2-diphenyl-ethylene was the major product.¹²

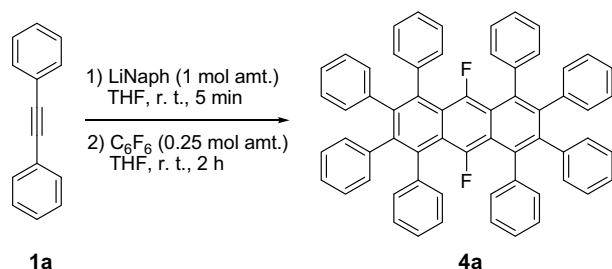
Then, we examined the reaction of **2a** prepared in situ from **1a** with hexafluorobenzene. Thus, the treatment of **2a** with 1 equiv of hexafluorobenzene in THF followed by workup and chromatographic purification produced **3a** as a white solid in 30% yield.^{13,14} Similarly, starting from **1b** produced **3b** in 29% yield (Scheme 1).

Interestingly, during the purification of **3a**, a trace amount of **4a** was isolated as a byproduct. This result suggests that terminal fluorine-substituted ‘unsymmetrical’ naphthalene **3** and central fluorine-substituted ‘symmetrical’ anthracene **4** could be synthesized with this one-pot procedure. As a test, the reaction between **2a** and 0.5 equiv of hexafluorobenzene was carried out and, as expected, **4a** was obtained in 7% yield as a bright-yellow solid¹⁵ (Scheme 2).

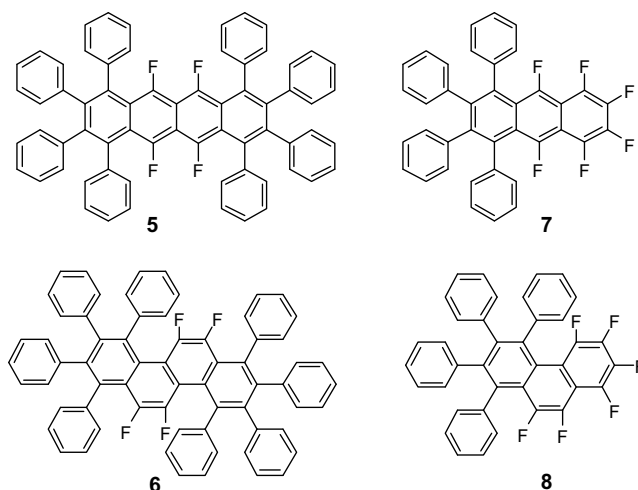
Encouraged by the results, we further investigated the reaction of **2a** with perfluoronaphthalene (C₁₀F₈), expecting that the procedure would provide a simple synthetic way to produce partially fluorinated tetracene **5**. However, chrysene **6** was produced as the major product when **2a** was treated with 0.5 equiv of C₁₀F₈, which was isolated as a yellow solid in 9% yield, while the expected **5** was not obtained. Similarly, anthracene **7** was not the major component in the mixed products when the reaction was carried between **2a** and the excess amount of C₁₀F₈. Compound **7** was only isolated in 2% yield together with 6% of phenanthrene **8**.



Scheme 1. Reagents and conditions: (i) LiNaph (1 mol amt.), THF, r. t., 5 min; (ii) C₆F₆ (excess), THF, rt, 2 h.



Scheme 2.



Structures of **5**, **6**, **7**, and **8**

Single crystals of **3a** and **4a** suitable for X-ray diffraction were obtained from THF/ethanol and CH₂Cl₂/hexane solution, respectively. Their molecular structure is shown in Figure 1. Compound **3a** crystallized in the orthorhombic space group *Pbca*. It has a partial face-to-face antiparallel π -stacking motif with the shortest C–C contact of 3.35 Å between two antiparallel molecules. The anthracene core of **4a** shows a coplanar conformation which is different from that of highly twisted decaphenylanthracene,¹⁶ which can be attributed to the reduced size of substituents at 9, 10 positions from phenyl groups to fluorine.

Though all attempts to prepare single crystal of **6**, **7**, and **8** failed, their structures could be determined by the analysis of ¹H, ¹⁹F NMR, high resolution mass spectra (HRMS), and UV–vis spectra.¹⁷ Compounds **7** and **8** have exactly the same molecular weight as indicated by their HRMS data. However, their ¹⁹F NMR spectra are distinguishable from each other. There are only three resonance signals for **7** but six for **8** in the ¹⁹F NMR spectra. This fact suggests the existence of six different types of fluorine atom in compound **8**, while **7** has more symmetric structure. Further elucidation of structures of **7** and **8** was also conducted by means of the combination of 2D homo- and heteronuclear experiments (see Supplementary data).

The data of UV–vis spectra also prove the assignment of molecular structures. The normalized UV–vis spectra and emission spectra of acene derivatives **3a**, **4a**, and **6–8** are shown in Figures 2 and 3, respectively. For the linear acene **3a**, **7**, and **4a**, both the absorption and emission maxima shift to longer wavelength with the increase of π -conjugation. The non-linear **6** and **8** show a similar trend. In the area of longer wavelength, the non-linear isomer **8** exhibits broader absorption peaks, while **7** has some of the fine vibronic structures. Notably, both **7** and **4a** show typical absorption band arising from anthracene backbone.

In summary, we report a convenient one-pot synthesis of highly aryl-substituted fluorinated acenes by the reaction

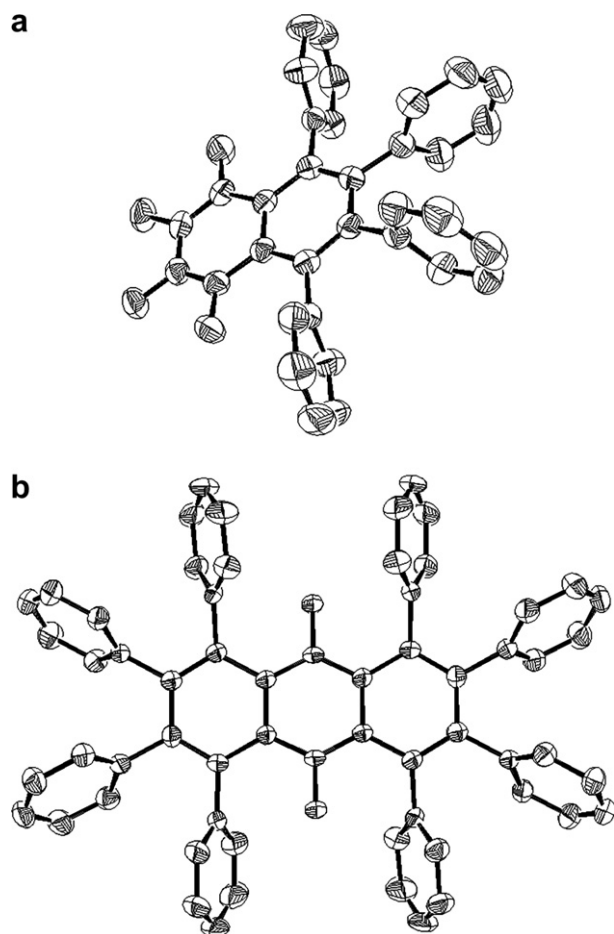


Fig. 1. ORTEP drawings of compounds (a) **3a** and (b) **4a** (50% probability for thermal ellipsoids. Hydrogen atoms are omitted for clarity).

of multi-fluorinated aromatics and 1,4-dilithio-1,2,3,4-tetraaryl-1,3-butadiene generated in situ from the reduction of diphenylacetylene derivatives with lithium naphthalenide. This new protocol is expected to provide a facile entry to a variety of substituted fluorine-containing

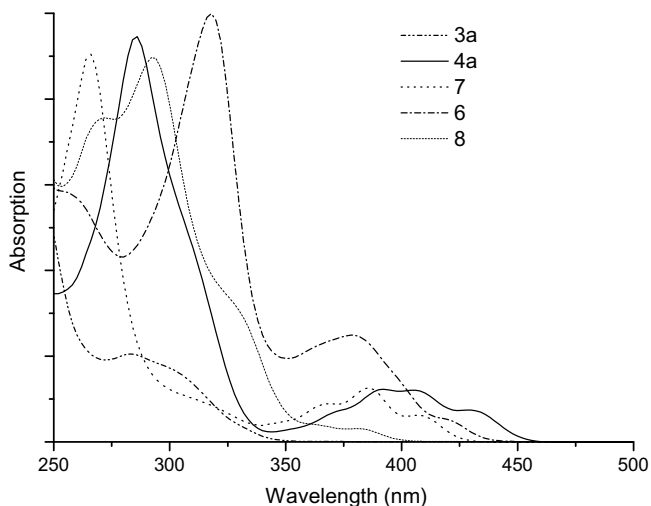


Fig. 2. Normalized absorption spectra of acene derivatives in THF.

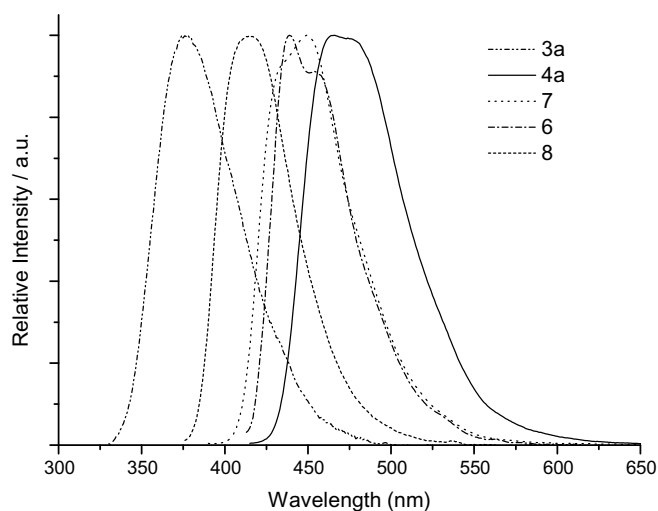


Fig. 3. Normalized emission spectra of acene derivatives in THF.

polycyclic aromatic hydrocarbons, which have potential application as new materials for organic electronic devices. Studies involving the optimization of the reaction conditions, examination of the applicable scale for acetylene derivatives, and the electronic properties of the present compounds are underway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.12.127](https://doi.org/10.1016/j.tetlet.2007.12.127).

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14. A typical procedure for the preparation of **3a**: A mixture of granular lithium (18.2 mg, 2.6 mmol) and naphthalene (336.3 mg, 2.6 mmol) in THF was stirred at room temperature (rt) for 4 h. To the resulting solution of lithium naphthalenide was added a solution of diphenylacetylene (311.6 mg, 1.75 mmol) in THF (4 mL) at room temperature. After stirring for 20 min, hexafluorobenzene (0.25 mL, 2.14 mmol) was added to the reaction mixture at room temperature. The reaction mixture was stirred for 1 h and then quenched with a saturated aqueous solution of NH_4Cl . The mixture was extracted with either ethyl ether or ether. The organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting mixture was passed through a silica gel column with petroleum ether ($R_f = 0.2$) as an eluent, followed by further purification by recrystallization (THF/ethanol) to give 133.2 mg of **3a** in 30% yield as a colorless crystal. Mp 259–260 °C. ^1H NMR (600 MHz, CDCl_3 , ppm) δ 6.73–6.75 (m, 4H), 6.78–6.85 (m, 6H), 7.12–7.17 (m, 10H); ^{19}F NMR (400 MHz, CDCl_3 , ppm) δ –136.40, –159.01; ^{13}C NMR (150.9 MHz, CDCl_3 , ppm) δ 142.20, 140.09, 138.87, 134.69, 130.87, 129.79, 127.01, 126.55, 126.51, 125.70, 118.85; HRMS (EI): Calcd for $\text{C}_{34}\text{H}_{20}\text{F}_4$: 504.15011. Found: 504.15005 (M^+). Crystallographic data: $\text{C}_{34}\text{H}_{20}\text{F}_4$, FW = 504.50, crystal dimension $0.52 \times 0.31 \times 0.17 \text{ mm}^3$, orthorhombic, space group *Pbca*, $a = 6.6985(13) \text{ \AA}$, $b = 22.946(5) \text{ \AA}$, $c = 32.459(7) \text{ \AA}$. $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$. $V = 4989.0(17) \text{ \AA}^3$. $Z = 8$, $D_c = 1.343 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.098 \text{ mm}^{-1}$, $T = 295$ (2) K, $F(000) = 2080$, $2\theta_{\text{max}} = 55^\circ$. 36,938 Reflections measured, of which 5573 was unique ($R_{\text{int}} = 0.0414$). Final $R_1 = 0.0708$ with $wR_2 = 0.2150$ for 3709 reflections with $I > 2\sigma(I)$.
15. **Compound 4a**: This compound was prepared essentially in the same manner as described for **3a** in 7% yield except for using 0.5 equiv of C_6F_6 . Bright-yellow solid. Mp $>300^\circ\text{C}$ ^1H NMR (600 MHz, CD_2Cl_2 , ppm) δ 6.70–6.71 (m, 4H), 6.76–6.83 (m, 16H), 6.97–7.05 (m, 20H); HRMS (EI): Calcd for $\text{C}_{62}\text{H}_{40}\text{F}_2$: 822.3098. Found: 822.3093 (M^+). Crystallographic data: $\text{C}_{62}\text{H}_{40}\text{F}_2$, FW = 822.94, crystal dimension $0.18 \times 0.16 \times 0.08 \text{ mm}^3$, monoclinic, space group *P2(1)/c*, $a = 6.477(3) \text{ \AA}$, $b = 15.423(8) \text{ \AA}$, $c = 21.836(11) \text{ \AA}$. $\alpha = 90.00^\circ$, $\beta = 93.678^\circ$, $\gamma = 90.00^\circ$. $V = 2176.9(19) \text{ \AA}^3$. $Z = 2$, $D_c = 1.255 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.077 \text{ mm}^{-1}$, $T = 294$ (2) K, $F(000) = 860$. 23,780 Reflections measured, of which 4410 was unique ($R_{\text{int}} = 0.000$). Final $R_1 = 0.0824$ with $wR_2 = 0.1840$ for 2670 reflections with $I > 2\sigma(I)$.
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17. **Compound 3b**: White solid. Mp 252–254 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.00 (s, 6H), 2.20 (s, 6H), 6.51–6.57 (m, 8H), 6.87–6.93 (m, 8H); ^{19}F NMR (400 MHz, CDCl_3) δ –135.685 (m, $J = 1.88 \text{ Hz}$), –158.735 (m, $J = 1.88 \text{ Hz}$); ^{13}C NMR (150.9 MHz, CDCl_3 , ppm) δ 142.50, 137.36, 136.09, 135.74, 134.74, 134.63, 130.68, 129.62, 127.67, 127.20, 119.03, 21.24, 21.04. HRMS (EI) Calcd for $\text{C}_{38}\text{H}_{28}\text{F}_4$: 560.2127. Found: 560.2133 (M^+). **Compound 6**: Yellow solid. Mp $>300^\circ\text{C}$. ^1H NMR (400 MHz, $\text{C}_4\text{D}_8\text{O}$) δ 6.70–6.73 (m, 4H), 6.74–6.80 (m, 10H), 6.85–6.86 (m, 6H), 6.98–7.08 (m, 20H); ^{19}F NMR (400 MHz, THF, ppm) δ –130.22 (d, $J = 7.53 \text{ Hz}$), –138.64 (d, $J = 7.53 \text{ Hz}$); HRMS (EI) Calcd for $\text{C}_{66}\text{H}_{40}\text{F}_4$: 908.3066. Found: 908.3077 (M^+). **Compound 7**: Yellow solid. Mp 291–293 °C ^1H NMR (600 MHz, CDCl_3 , ppm) δ 6.74–6.75 (m, 4H), 6.81–6.83 (m, 6H), 7.15–7.17 (m, 10H), ^{19}F NMR (400 MHz, CDCl_3 , ppm) δ –111.74 (d, $J = 37.65 \text{ Hz}$), –145.975 (d, $J = 39.53 \text{ Hz}$), –157.16; HRMS (EI): Calcd for $\text{C}_{38}\text{H}_{20}\text{F}_6$: 590.1469. Found: 590.1475 (M^+). **Compound 8**: White solid. Mp 219–221 °C ^1H NMR (600 MHz, CDCl_3 , ppm) δ 6.64–6.69 (m, 4H), 6.81 (m, 2H), 6.87–6.94 (m, 6H), 7.01 (m, 2H), 7.08–7.14 (m, 6H); ^{19}F NMR (400 MHz, CDCl_3 , ppm) δ –123.82, –136.29, –148.38 (d, $J = 32.00 \text{ Hz}$), –149.65 (m, $J = 23.53 \text{ Hz}$), –156.29 (t, $J = 18.82 \text{ Hz}$), –158.98 (t, $J = 22.59 \text{ Hz}$); HRMS (EI): Calcd for $\text{C}_{38}\text{H}_{20}\text{F}_6$: 590.1469. Found: 590.1473 (M^+).