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Direct Functionalization of Polycyclic Aromatics via Radical Perfluoroalkylation

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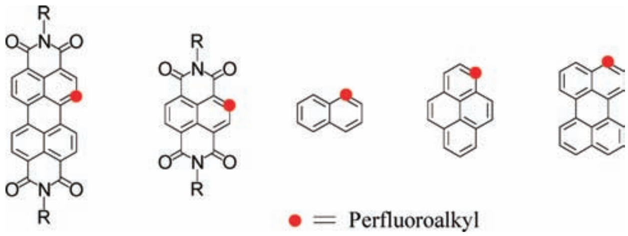
ABSTRACT



Direct functionalization of electron-deficient and electron-rich polycyclic aromatics via copper-mediated radical perfluoroalkylation was achieved in high yields.

Due to their remarkable electro-optical properties,[1] perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs) have received a great deal of attention as promising organic n-type semiconductors which have found applications such as light-harvesting arrays,[2] field effect transistors,[3] light-emitting diodes,[4] and photovoltaics[5] in the past decades. Naphthalene bis(dicarboximide)s (NBIs) were also identified recently as key polymer building blocks to ensure a strong electron-depleted electronic structure.[6] Chemical modifications both at imide groups and in bay regions are two different successful synthetic strategies for rylene bisimide derivatives. However, the dramatic change of optical and electronic properties can only be achieved by the bay-functionalization because of nodes in the HOMO and LUMO orbitals at the imide nitrogen atoms.

One of the key design principles for air-stable n-type rylene-based semiconductor materials is to incorporate strong electron-withdrawing groups. Core-cyanated and *N*-fluoroalkylated PBI and NBI derivatives have been reported to exhibit high n-type mobilities and air stability.[7] Core-fluorinated perylene bisimides have also been synthesized and achieved promising n-type semiconducting properties.[8] Recently we have reported a highly efficient synthetic methodology toward the bis-perfluoroalkylated perylene bisimides from regioisomerically pure 1,7-dibromo PBIs.

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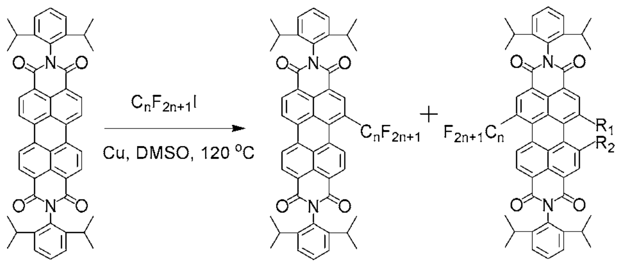
Furthermore, the organic field effect transistors (OFETs) incorporating this new n-type semiconductor show remarkable air-stability and good charge carrier mobility.[9] While these approaches are attractive, new methods for the direct perfluoroalkylation of polycyclic aromatics remain highly desirable in terms of atom and step economy by avoiding a “prefunctionalization” process.

In the past several decades, many efforts have been made to direct C−H functionalization/C−C bond formation,[10] which provides a viable alternative to a traditional cross-coupling reaction. To date, great elegant progress has been achieved for electron-rich arenes and heterocycles with a directing group that can be ortho-functionalized by aryl or alkyl halides, boronates, and olefins under palladium,[11] ruthenium,[12] or rhodium[13] catalysis. Direct C−H bond transformation of unreactive arenes is, however, still a challenge. Very recently, Shinokubo and his co-workers have reported success with Ru-catalyzed alkylation and arylation of PBIs;[14] meanwhile, we have also reported direct alkylation of PBIs by palladium-catalyzed C−H functionalization.[15] Herein, we present the direct functionalization of electron-deficient and electron-rich polycyclic aromatics via copper-mediated radical perfluoroalkylation.

Initially, a highly electron-deficient perylene bisimide **1** was chosen as a model substrate for this study. Direct copper-mediated perfluoroalkylation of **1** with perfluoroalkyl iodides gives excellent yields of mono-core-perfluoroalkylated PBIs (Schemes 1, compounds **2** and **4**). It should be noted that monobrominated perylene bisimides are relatively not so easily available compared with dibrominated and tetrabrominated perylene bisimides, which makes it difficult to introduce a single function group to the bay region. What is interesting is that the perfluoroalkyl group is regioselectively introduced to the bay region. Meanwhile, 1,6- and 1,7-perfluoroalkylated PBIs were also obtained in about 20% yields in a ratio of 1:5.

Scheme 1. Regioselective Perfluoroalkylation of PBI



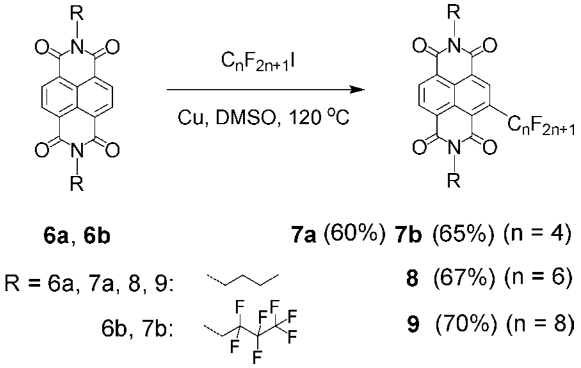
1

2 (57%) (n = 4) **3** (18%) (n = 4)

4 (60%) (n = 8) **5** (14%) (n = 8)

3a, 5a (R_1 = H, R_2 = C_nF_{2n+1})
3b, 5b (R_1 = C_nF_{2n+1}, R_2 = H)

Scheme 2. Perfluoroalkylation of NBI

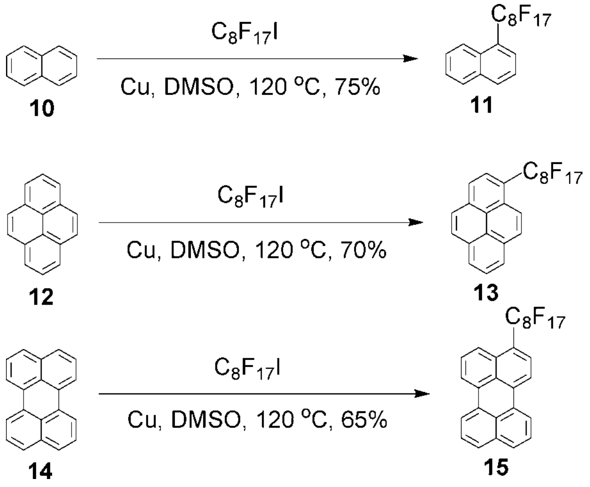


6a, **6b** **7a** (60%) **7b** (65%) (n = 4)

R = 6a, 7a, 8, 9: **8** (67%) (n = 6)

6b, 7b: **9** (70%) (n = 8)

Scheme 3. Regioselective Perfluoroalkylation of Electron-Rich Molecules



10 **11**

12 **13**

14 **15**

Under the optimized reaction conditions above, the substrate scope was also explored. Recently, Watson reported Stille coupling of regioisomerically pure dibromonaphthalene bisimides (NBIs) with various stannylated thiophene-based

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monomers that yields high molecular weight donor−acceptor conjugated polymers.[6b] Yan demonstrated a highly soluble and printable n-channel NBI−thiophene copolymer exhibiting unprecedented OTFT characteristics (electron mobilities up to 0.45−0.85 cm^2 V^{-1} s^{-1}) under ambient conditions in combination with Au contacts and various polymeric dielectrics.[6c] Direct copper-mediated perfluoroalkylation of naphthalene bis(dicarboximide)s with perfluoroalkyl iodides gave excellent yields of mono- perfluoroalkylated NBIs. Different perfluoroalkyl iodides (iodononafluorobutane, 1-iodoperfluorohexane, and 1-iodoperfluorooctane) were chosen to react with NBI and the isolated yield was from 60% to 70%. However, it should be mentioned that there is no desired product detected, when bromo NBIs react with perfluoroalkyl iodides under the same conditions.

A great variety of perfluoroalkylated polycyclic aromatics, such as naphthalene, pyrene, and perylene, could be prepared via this method with high yields. What should be noticed here is that perfluoroalkyl chain was regioselectively introduced to the 1 position of naphthalene and pyrene, and the 3 position of perylene.

To assess the effect of the perfluoroalkyl groups on the molecular order in the solid state, attempts were devoted to single-crystal growth. Ultimately, crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of an ethanol solution of **3b** and a dichloromethane solution of **13**, respectively. The molecular structures of **3b** and **13** are depicted in Figure 1.

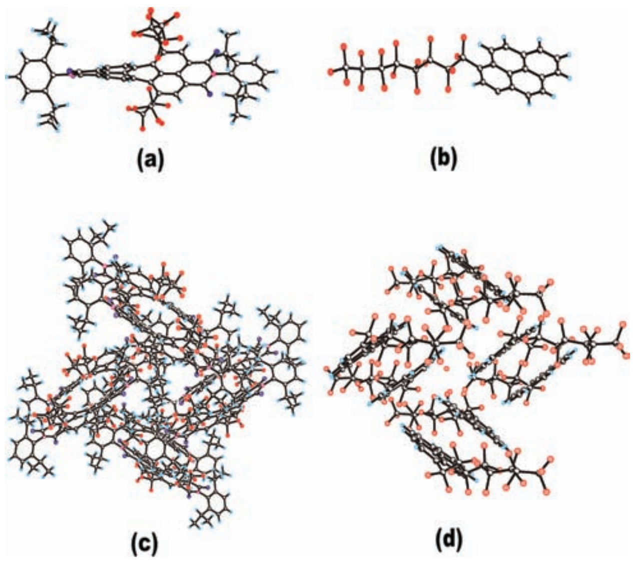

Figure 1. Molecular structure of **3b** (a) and **13** (b). Crystal packing of **3b** (c) and **13** (d).

Four molecules of **3b** and **13** were found in the unit cell. As shown in Figure 1a, owing to the steric encumbrance effect of perfluoroalkyl substituents, the perylene cores are highly twisted as expected. The twisting of the central six-membered ring was unsymmetrical with dihedral angles of 28.5° and 29.9°. The crystals of **3b** and **13** have been found and arranged in a sandwich herringbone packing including dimeric species probably due to the notable dipole−dipole interaction, and not the stacks along the α-axis of the unit cell for 1,7-perfluoroalkyl-substituted PBIs.[9] The subtle changes in molecular structures lead to dramatically different packing arrangements in the solid state and were also expected to have a strong influence on the charge transporting properties.

The summarized electro-optical data of perfluoroalkylated polycyclic aromatics are shown in Table 1, and the UV−vis absorption, fluorescence spectra, and cyclic voltammograms were given in the Supporting Information.

Table 1. Electro-optical Properties of Perfluoroalkylated Polycyclic Aromatics

	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	$E_1{}^a$	$E_2{}^a$
2	521	58 219	538	−0.82	−1.11
3a	510	55 329	526	−0.67	−0.99
3b	512	45 986	536	−0.68	−1.03
4	521	53 757	537	−0.82	−1.09
5a	510	57 220	526	−0.67	−0.99
5b	512	56 351	539	−0.68	−1.04
6a	380	31 475	360	−1.05	−1.53
7a	384	25 298	360	−0.89	−1.46
8	384	23 833	359	−0.87	−1.47
9	384	22 375	360	−0.86	−1.49
6b	376	32 478	361	−0.88	−1.37
7b	380	23 191	361	−0.68	−1.22
11			358		
13	346	37 489	377		
15	446	28 410	460		

[a] Half-wave potentials (in V vs Fc/Fc$^+$) measured in a 0.1 M solution of Bu_4NPF_6 in dichloromethane with a scan rate of 50 mV/s.

The absorption spectra of **2**−**5** show well-defined vibronic fine structures of the S_0−S_1 transitions with maxima at 521 nm for **2** and **4**, 510 nm for **3a** and **5a**, and 512 nm for **3b** and **5b**, hypsochromically shifted by 5, 16, and 14 nm, respectively, in comparison with parent PBI derivatives, probably due to the electron-withdrawing effect of perfluoroalkyl substituents.

The absorption maxima of 1,6-perfluoroalkylated PBIs (**3b** and **5b**) bathochromically shifted only 2 nm in comparison with that of 1,7-perfluoroalkylated PBIs (**3a** and **5a**); however, 1,7-perfluoroalkylated PBIs show a higher absorption coefficient than 1,6-perfluoroalkylated PBIs. Mono- and bis-perfluoroalkylated PBIs presented here possess Stokes shifts between 16 and 27 nm, and exhibit very high fluorescence quantum yields (0.86−0.92). The absorption spectra maxima of perfluoroalkylated NBI (**7a** and **7b**) bathochromically shifted by 4 nm in comparison with **6a** and **6b**, and the absorption maxima spectra of **13** and **15** bathochromically shifted by 8 nm in comparison with **12** and **14**.

Cyclic voltammograms of perfluoroalkylated PBIs and NBIs in CH_2Cl_2 show two reversible reduction waves. The half-wave reduction potentials vs Fc/Fc$^+$ are −0.82 and

−1.11 V for **2**, −0.67 and −0.99 V for **3a**, −0.68 and −1.03 V for **3b**, −0.89 and −1.46 V for **7a**, and −0.68 and −1.22 V for **7b** respectively (Table 1). Both first and second reduction waves appeared at higher potentials with comparison to parent PBIs and NBIs, indicating that core-perfluoroalkylation induces strong electron-accepting ability. Due to the additional electron affinity of fluoroalkyl chains at the *N*-substituents, the reduction potentials of **7b** are less negative than those of **7a**. The absorption, emission spectra, and cyclic voltammograms are not significantly influenced by the number of fluorine substituents when the fluorinated alkyl chain contains more carbon atoms.

Perfluoroalkyl iodides have been widely utilized as sources of perfluoroalkyl radicals. The free-radical chain addition to alkenes and the homolytic aromatic substitution by thermolysis are well-known processes.[16] To gain some understanding of the investigated perfluoroalkylation reaction of polycyclic aromatics, radical scavenger, TEMPO, was added to the reaction mixture in the same equivalent as perfluoroalkyl iodides. The reaction was completely inhibited and just returns the reactant, which supports the radical perfluoroalkylation mechanism.

In conclusion, a copper-mediated regioselective perfluoroalkylation process of highly electron-deficient rylene dyes and electron-rich polycyclic aromatics has been achieved. The generality and unique properties of perfluoro-alkylated polycyclic aromatics may expand the scope of this reaction to more academic and industrial applications.

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Supporting Information Available: Experimental procedure and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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