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Efficient Synthesis of Regioisomerically Pure Bis(trifluoromethyl)-Substituted 3,4,9,10-Perylene Tetracarboxylic Bis(benzimidazole)

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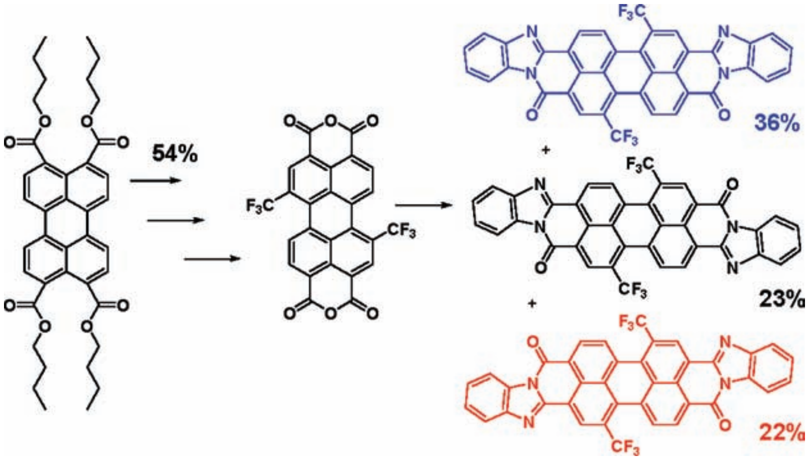
ABSTRACT



By a new strategy, two trifluoromethyl groups were efficiently introduced to highly insoluble n-type semiconductor 3,4,9,10-perylene tetracarboxylic bis(benzimidazole) (PTCBI), and for the first time we obtained three pure regioisomers of bis(trifluoromethyl)-substituted PTCBI, whose optical properties are different from one another.

3,4,9,10-Perylene tetracarboxylic bis(benzimidazole) (PTCBI) played an important role in the field of organic semiconductors. In 1986, two-layer solar cells based on PTCBI and copper phthalocyanine were reported for which the power conversion efficiency was up to 0.95%,[1] which was a major breakthrough in organic solar cells. In 2000, solar cells based on PTCBI with a power conversion efficiency up to 2.4 ± 0.3% were obtained.[2] PTCBI was also used as the electron-acceptor layer in three-layer organic solar cells[3] and as the n-doped electron transport layer in p-i-n solar cells.[4] Despite its glorious history, PTCBI has not been extensively investigated in recent years. In contrast, its sisters,

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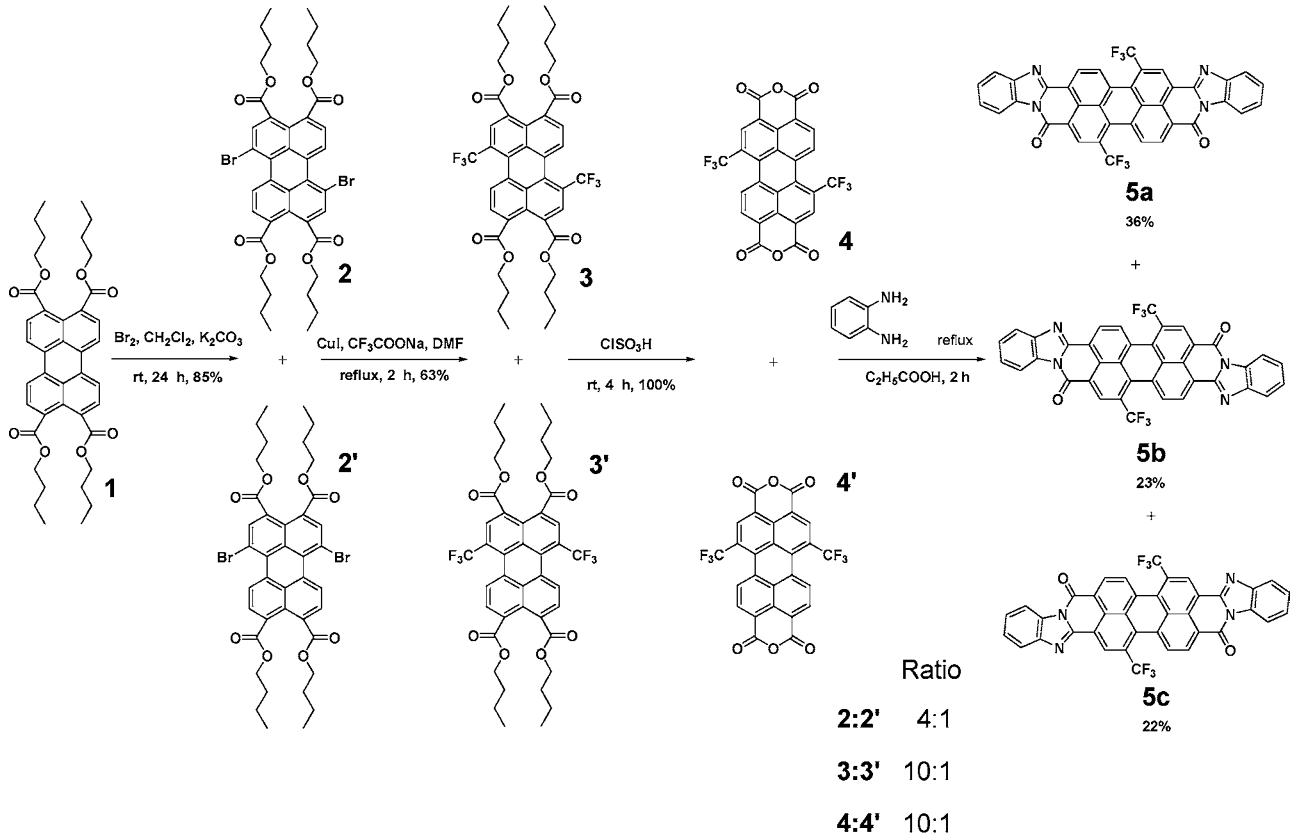
Scheme 1. Synthesis of Bis(trifluoromethyl)-Substituted PTCBI



perylene bisimides, have attracted much current attention. Such a situation is mainly ascribed to two unsolved problems brought about by the insolubility of PTCBI in common organic solvents. On the one hand, so far devices based on PTCBI derivatives have utilized only mixtures of isomers rather than pure compounds, since the synthesis and separation of specific regioisomers of PTCBI derivatives are not achievable. On the other hand, direct modification of PTCBI is unachievable, since some synthetic strategies for preparing functional perylene bisimides derivatives were not suitable for PTCBI's modification.

For the sake of developing a high performance n-type organic semiconductor, we are interested in introducing perfluoroalkyl groups to PTCBI, as perfluoroalkyl groups can efficiently increase air stability and electron mobility in many organic semiconductor platforms.[5] Even the trifluoromethyl group, the smallest among perfluoroalkyl groups, also exerts such effects, which is confirmed in our recent investigation on bis(trifluoromethyl)-substituted triphenodioxazines.[6] Particularly, almost at the same time, we[7] and Wang et al.[8] attached perfluoroalkyl groups to the aromatic core of perylene bisimides via directly coupling of bromo-substituted perylene bisimides with perfluoroalkyl iodide and obtained an air-stable n-type semiconductor. Though we expect that perfluoroalkyl-substituted PTCBI are good n-type semiconductors, direct perfluoroalkylation on a perylene core is impractical for PTCBI because of its poor solubility. So, a new strategy should be adopted.

Herein, for the first time, two trifluoromethyl groups were introduced to the perylene unit of PTCBI and three regioisomerically pure PTCBI derivatives were obtained. Different from previous syntheses of perfluoroalkyl-substituted perylene bisimides, our new strategy featured trifluoromethylation of

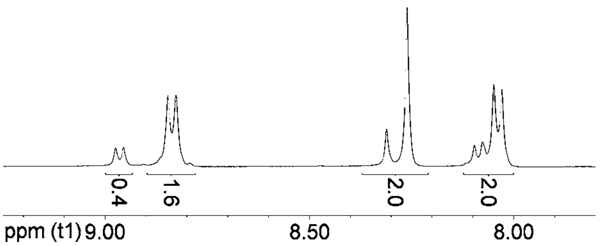


Figure 1. Low-field section of ^1H NMR spectrum of mixture of compound **2** and **2′** in CDCl$_3$.

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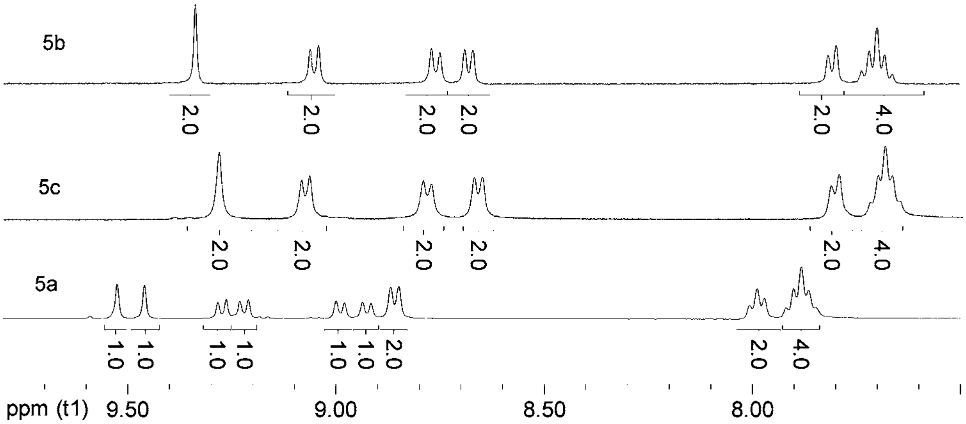

Figure 2. ^{1}H NMR spectrum of compounds **5a** (bottom), **5b** (top), and **5c** (middle) in CF_3COOD.

a highly soluble intermediate and its further highly efficient transformation to target compounds, as illustrated in Scheme 1.

To increase the solubility of reactant used in the trifluoromethylation, highly soluble intermediate 1,7-dibromo-3,4,9,10-tetra(*n*-butoxy-carbonyl)-perylene (**2**) was synthesized via bromination of 3,4,9,10-tetra(*n*-butoxy-carbonyl)-perylene (**1**) at room temperature. In this step, 1,6-dibromo-3,4,9,10-tetra(*n*-butoxy-carbonyl)-perylene (compound **2′**) was inevitable and could not be separated from compound **2** through silica gel column chromatography. NMR spectroscopy (400 MHz) (shown in Figure 1) indicated the ratio of **2** to **2′** was 4:1. Similarly, bromination of perylene-3,4,9,10-tetracarboxylic dianhydride in oleum also produced 1,7-dibromo and 1,6-dibromo isomers in a 4:1 ratio, which was first confirmed in 2004 by Würthner et al. with 600 MHz NMR spectroscopy.[9]

The trifluoromethylation of the mixture of compound **2** and **2′** led to a mixture of bistrifluoromethylated tetra(*n*-butoxy-carbonyl)-perylene with 1,7-isomer (compound **3**) and 1,6-isomer (compound **3′**) in a ratio of 10:1. Hydrolysis of mixture of **3** and **3′** in chlorosulfonic acid was carried out smoothly at room temperature and resulted in 100% yield of corresponding 1,7- and 1,6-bis(trifluoromethyl)-substituted dianhydride regioisomers with a 10:1 ratio. The product can be easily obtained by adding the reaction mixture to ice and filtering. This hydrolysis for perylene dianhydride is advantageous over previous method in which perylene bisimides were hydrolyzed in strong basic solution at high temperature for long time. More importantly, previous method may be unsuitable for trifluoromethyl-substituted perylene dianhydride, since trifluoromethyl group on many kinds of aromatic core are not tolerant to such harsh conditions.[10]

The condensation of bis(trifluoromethyl)-dianhydride (mixture of compound **4** and **4′**) with 1,2-diaminobenzene in propanoic acid at reflux satisfactorily led to target bis(trifluoromethyl)-substituted PTCBI, which can be separated by silica gel column chromatography. Theoretically, there should be three regioisomers originated from 1,7-bis(trifluoromethyl)perylene dianhydride, and all of them were obtained. ^{1}H NMR can unambiguously differentiate the three regioisomers (shown in Figure 2), and one isomer with an unsymmetrical structure is identified to be compound **5a**. For another isomer, the ^{13}C NMR spectrum shows that the carbon atom attached to nitrogen atom by a double bond resonates at 147.1 ppm; in the HMBC spectrum (Supporting Information), this carbon atom exhibits a strong coupling signal with the proton showing a singlet peak signal at 9.27 ppm, so this isomer is identified to be compound **5c**. The remaining one is compound **5b**. Compounds **5a**−**5c**, with isolated yields of 36%, 23%, and 22%, respectively, were all characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS. In the column, several other fluorescent compounds were observed, but they were not identified because of their trace amounts. They may be ascribed to 1,6-isomers or some byproducts.

Different from highly insoluble PTCBI, compound **5a**−**5c** are soluble in toluene, DMF, dichloromethane, etc., which makes purification with column chromatography and optical test possible. The increased solubility is mainly ascribed to the “fluorine effect”[11] of the trifluoromethyl group, and meanwhile a possible twist of the perylene core, existing in previous core-substituted perylene bisimides,[8,9] may partly enhance the solubility.

The absorption and fluorescence spectrum of compound **5a**−**5c** in dichloromethane are shown in Figure 3, and optical data for the compounds are given in Table 1. All three regioisomers exhibit absorption bands split into two contiguous peaks. Absorption bands of compound **5b** and **5c** have similar shapes in which the peaks at longer wavelengths are a little higher than the ones at shorter wavelengths, and both peaks of **5b** are at positions (around 550 and 590 nm) similar to the corresponding ones of **5c**. Despite the above similarities, compound **5b** has much higher absorption intensity

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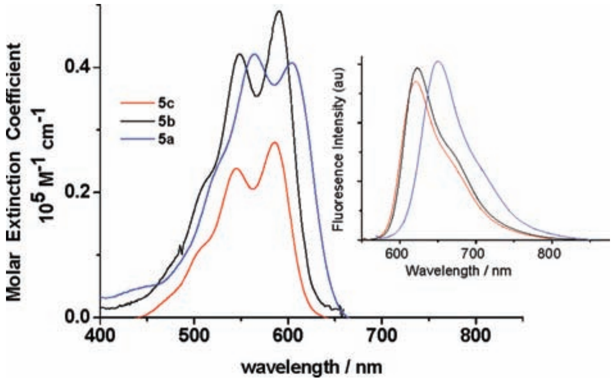

Figure 3. UV−vis absorption (left) and fluorescence emission (right) spectrum of compound **5a**−**5c** in dichloromethane.

compared to that of **5c**. The maximum molar extinction coefficient of **5b** is up to 49 000, which is nealy 2-fold that of **5c**. In the absorption spectrum of compound **5a**, the shorter wavelength peak is a little higher in intensity than the other, which is in contrast to the cases of **5b** and **5c**, and the two peaks of **5a** are considerably red-shifted by 15−20 nm, relative to those of **5b** and **5c**. The absorption capapbility of compound **5a** is approximative to that of **5b** and is much stronger than that of **5c**. As shown in Figure 4, **5a**−**5c** show a similar absorption profile in the solid state, and the absorption range of **5a** is red-shifted by roughly 30 nm relative to those of **5b** and **5c**. Calculated optical band gaps of **5a**−**5c** in solids are 1.68, 1.77, and 1.74 eV respectively.

Table 1. UV−vis Absorption and Fluorescence Emission Properties of Compound **5a**−**5c** in Dichloromethane

	$\lambda_1{}^a$ (nm)	$\varepsilon_1{}^a$ (M^{-1} cm^{-1})	$\lambda_2{}^b$ (nm)	$\varepsilon_2{}^b$ (M^{-1} cm^{-1})	λ_{em} (nm)	S^c (nm)	$\varphi_{fl}{}^d$
5a	564	42 100	604	40 700	650	86	0.14
5b	548	42 100	590	49 000	623	33	0.15
5c	545	23 800	586	28 000	621	35	0.18

[a] The first absorption peaks and corresponding molar extinction coefficients. [b] The second absorption peaks and corresponding molar extinction coefficients. [c] Stoke shift. [d] Determined with Rhodamine 6G as reference.[12]

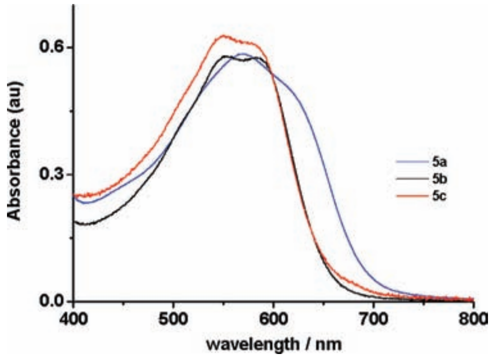

Figure 4. UV−vis absorption of compound **5a**−**5c** in the solid state.

In addition, **5b** and **5c** have the similar emission spectra with emission peaks around 620 nm; the emission peak of **5a** exhibits remarkable red shift of nearly 30 nm relative to those of **5b** or **5c.** Obvious differences of their UV−vis absorption indicate different electron transition energies of the three regioisomers, and we believe it should be better to use regioisomerically pure PTCBI derivatives to fabricate devices in future.

In conclusion, by a new strategy featuring trifluoromethylation of a highly soluble intermediate and its further highly efficient transformation to bis(trifluoromethyl)-substituted PTCBI, three pure regioisomers of PTCBI derivatives were first obtained and well characterized. They display different optical properties, and further investigations on their applications are in progress.

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Supporting Information Available: Experimental procedures and full characterizations data. This material is available free of charge via the Internet at http://pubs.acs.org.

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