Synthesis of 1,3,6,8-Tetrakis(4-acetylsulfanyl-phenylethynyl)pyrene: A potential candidate for molecular wire application

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ABSTRACT

A synthetic route for the preparation and purification of a pyrene derivative - 1,3,6,8-Tetra(4-acetylsulfanyl-phenylethynyl)pyrene - is described. The fluorescence properties of the compound were recorded.

INTRODUCTION

Application of a single or an organized ensemble of organic molecules in the areas of molecular photonics and electronics is in the frontiers of chemical research. Structure based identification of organic molecules for specific function, development of synthetic methodology for the efficient synthesis and characterization are in the domain of synthetic organic chemistry. Pyrene derivatives have achieved immense importance in this regard. Pyrene, one of the polycyclic aromatic hydrocarbons (PAH) was first isolated a century ago from coal (Laurent, 1837). Its photophysical properties (Winnik, 1993) made pyrene and its derivatives highly desirable fluorescence probes, usable in many applications. More recent examples includes the usage of pyrene as fluorescent labels for kinetic studies (Olmos et al., 2005), labeling oligonucleotides (Yamana et al., 2002) for DNA studies, reflected as well in DNA hybridization (Ebata et al., 1995). Bis-pyrene is used in some similar functions, labeling molecular beacons (Yamana et al., 2006). Even more recent is the synthesis of a pyrene-salicylaldimine, another pyrene derivative which exhibits fluorescence apt for labels (Yilmaz, 2007).

Despite the photophysical properties of pyrene, there exist several disadvantages to it. One of these drawbacks would be pyrene’s absorption and emission wavelength, which is limited to the UV region. For many of the applications pyrene derivatives are suitable for, it would be preferable if the fluorescence probe absorbs and emits at higher wavelengths towards the visible light spectrum. This is especially so when probing biological membranes, as some biomolecules may emit intrinsic fluorescence which can overlap that of pyrene, including many organic light-emitting devices (OLEDs) (Aziz and Popovic, 2004). Therefore, to induce a bathochromic shift in the fluorophobe, one method is by introducing unsaturating functional groups to its core, pyrene.

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Here we are reporting the design and synthesis of a new 1,3,6,8- tetrasubstituted pyrene (1) with the aim of applying it as molecular wire. Molecular wires of several nanometer length based on acetylene chemistry are reported in literature. Hence 1 can be used as multi terminal wire where the central pyrene ring acts as the contact junction for the molecular wires made of acetylene. The terminal –SAc groups serve as the contact points to the external circuit.

EXPERIMENTAL

(A) 1,3,6,8-Tetramethylpyrene (1): Bromine (3.50 g, 22.0 mmol) was added dropwise, with stirring, to a solution of pyrene (1.0 g, 4.90 mmol) in nitrobenzene (20 mL) at 120 °C. The reaction mixture was kept at 120 °C for 4 h. The mixture was then cooled to room temperature, to afford a pale green precipitate. This was filtered, and the solid was washed with copious amount of ethanol (150 mL). The residue was dried under vacuum to afford 1 (2.31 g, 90.2% yield). (Scheme 1)

(B) 1,3,6,8-Tetakis(trimethylsilyl)pyrene (2): A 3-necked round-bottomed-flask was purged with nitrogen gas for 5 minutes, before adding diisopropylamine (10 mL) and tetrahydrofuran (10 mL). The flask was purged for another 10 minutes. Compound 1 (500 mg, 0.965 mmol), Pd[PPh3]2Cl2 (33.5 mg, 0.048 mmol), CuI (9.0 mg, 0.048 mmol), PPh3 (25 mg, 0.096 mmol) were then quickly added, and the mixture was purged for 5 minutes. Trimethylsilylacetylene (0.820 mL, 5.785 mmol) was then injected via syringe. The reaction mixture was heated at 65 °C under nitrogen atmosphere for 12 h. The mixture was transferred to a 1-neck-r.b.f. The solvent was removed under vacuum and the insoluble product was subjected to column chromatography (silica gel with hexane as eluent). Purification yields the desired compound, compound 2 as a red orange solid (0.18 g, 31.3% yield). (Scheme 1)
(C) **1,3,6,8-Tetraethynylpyrene (3):** A solution of 2 (1.0 g, 1.70 mmol) in methanol (20 mL) was treated with K$_2$CO$_3$ (1.88 g, 13.6 mmol). The mixture was stirred at room temperature (30 °C) for 12 hours. The mixture was filtered and washed with water. Compound 3 was obtained as a yellow solid. (0.40 g, 77.5 % yield). (Scheme 1)

(D) **1,3,6,8-Tetra(4-acetylsulfanyl-phenylethynyl)pyrene (4):** A 3-necked round-bottomed-flask was purged with nitrogen gas for 5 minutes, before adding diisopropylamine (30 mL) and tetrahydrofuran (30 mL). The flask was purged for another 10 minutes. Compound 3 (93.8 mg, 0.315 mmol), 4-acetylsulfanyl-iodobenzene (700 mg, 2.52 mmol), Pd[PPh$_3$]$_2$Cl$_2$ (43.2 mg, 0.062 mmol), CuI (24.4 mg, 0.130 mmol), PPh$_3$ (67.0 mg, 0.257 mmol) were then quickly added. The reaction mixture was heated at 55 °C under nitrogen atmosphere for 30 hours. The mixture was transferred to a 1-neck-r.b.f. The solvent was removed under vacuum and the insoluble product was subjected to column chromatography (silica gel, hexane/DCM 85:15). Purification yields the desired compound 4 (0.099 g, 35.0 % yield). (Scheme 1)

**RESULTS AND DISCUSSION**

1,3,6,8-Tetabromopyrene is obtained via exhaustive bromination on pyrene, and the synthesis had a good yield. Following the synthesis of tetrabromopyrene, it was subjected to Sonogashira ethynylation reaction (Sonogashira *et al.*, 1975) with trimethylacetylene, forming 1,3,6,8-tetrakis(trimethylsilylthyynyl)pyrene 2 (Scheme 1). This compound is purified by column chromatography, and is deprotected by K$_2$CO$_3$ under mild conditions to yield 3, tetraethynylpyrene, a very stable solid which could be stored at room temperature.

Due to its stability, tetraethynylpyrene (3) was reacted for 30 hours at 55 °C with 4-acetylsulfanyl-iodobenzene to form 1,3,6,8-tetra(4-acetylsulfanyl-phenylethynyl)pyrene 4 under Sonogashira conditions.

The fluorescence spectra of 1,3,6,8-tetra(4-acetylsulfanyl-phenylethynyl)pyrene compared to pyrene also shows a great bathochromic and hyperchromic shift. The peaks are observed within 400-700 nm, the visible light region.

![Figure 1: Fluorescence spectra of pyrene (---) and 1,3,6,8-tetra(4-acetylsulfanyl-phenylethynyl)pyrene (--)](image)
CONCLUSIONS

An efficient method to synthesize a new pyrene derivative has been described. The extended conjugation on 1,3,6,8-tetra(4-acetylsulfanyl-phenylethynyl)pyrene serve to shift the wavelength of fluorescence absorption and emission to the visible region of the electromagnetic spectrum. There is also a hyperchromic shift, and the compound is highly applicable as a fluorescence probe and molecular wire.

REFERENCES