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Article

Chemistry

Cyclopenta-fused perylene: a new soluble, stable and functionalizable rylene building block

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Abstract We report a facile synthesis of a [1,12-*b*,*c*,*d*]-cyclopenta-fused perylene **5** from the parent perylene via a formylation-oxidative esterification–nucleophilic addition-followed-by-Friedel–Crafts alkylation strategy. Compared with the perylene, dye **5** exhibits much higher solubility, smaller energy gap, and can undergo regio-selective bromination at the *peri*-positions. Compared with the *N*-annulated perylene **8**, compound **5** shows lower HOMO energy level and is more stable in air. Therefore, **5** can be regarded a new versatile building block for the development of high-order soluble and stable rylenes and various perylene-based functional materials.

Keywords Organic dye · Rylene · Perylene · Polycyclic aromatic hydrocarbon

1 Introduction

Perylene is an important pigment/dye and semiconductor for many technical applications [1]. It is also an important building block to construct higher-order rylenes such as quaterrylene, hexarylene and octarylenes [2]. In many cases, the chemistry was limited by its poor solubility and the lack of regio-selectivity. Recently, annulation of a heteroatom such as sulfur [3], selenium [3] and nitrogen [3, 4] onto the bay region of perylene (Fig. 1) has been successfully performed, and the new heteroatom-annulated perylenes displayed distinct electronic and self-assembling properties in comparison with the parent perylene. As a result, new materials for high-performance field-effect transistors [5], solar cells [6–8], near-infrared (NIR) dyes [9–14] and open-shell singlet diradicaloids [15–18] have been developed. In spite of these successes, some constrains remain: (1) for the S/Se-annulated perylene, the poor solubility limits further functionalization and solution processing; (2) for the *N*-annulated perylene (NP), the solubility can be largely improved by incorporation of alkyl/aryl groups at the amine site, but strong aggregation still exists in solution, which is not desirable for the synthesis of higher-order rylenes as well as perylene-based sensitizers; in addition, the electron-rich character of NP makes the fused NP systems unstable in air. To solve all these problems, we believe that a [1,12-*b*,*c*,*d*]cyclopenta-fused perylene (CP) with a sp^3-carbon annulated at the bay region (Fig. 1) is a good choice based on the following considerations: (1) two aryl groups can be easily introduced to the carbo-site and suppress the dye aggregation, meanwhile solving the solubility problem; (2) like NP and fluorene, mono- or di-bromination could selectively take place at the two *peri*-positions near the cyclopenta-ring, which will open the opportunities for further functionalizations; (3) the sp^3-carbon atom annulated perylene is more electron deficient than the NP and is supposed to have a lower HOMO energy level compared with NP and should be more stable, which makes the CP-based higher-order rylenes or hybrid systems accessible in the future. However, the synthesis of the carbo-annulated CP is challenging and to the best of our knowledge has never been reported.

Electronic supplementary material The online version of this article (doi:10.1007/s11434-015-0839-3) contains supplementary material, which is available to authorized users.

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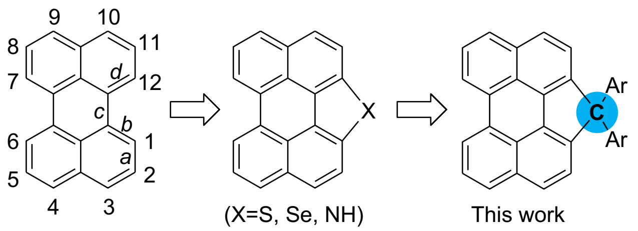

Fig. 1 (Color online) Molecular structures of perylene (including numbering), heteroatom-annulated perylene and cyclopenta-fused perylene

Herein, we report the simple synthesis of CP, its regioselective bromination, as well as its photophysical and electrochemical properties in comparison with the parent perylene and NP derivative.

2 Materials and methods

Dye **5** and its mono-/dibromo derivatives **6/7** were synthesized according to the synthetic scheme shown in Fig. 2. More details on the characterization data and methods are shown in Electronic Supplementary Materials (online).

2.1 Synthesis of **5**

The parent perylene **1** in dry dichloromethane (DCM) was submitted to formylation reaction with 1,1-dichlorodimethyl ether in the presence of $SnCl_4$. A suspension of perylene (3 g, 11.92 mmol) in CH_2Cl_2 (70 mL) was cooled to 0 °C in an ice bath under an argon atmosphere. $SnCl_4$ (2.88 mL, 24.6 mmol) was added in one portion, and then Cl_2CHOCH_3 (1.35 mL, 12.3 mmol) was added dropwise over 1 h, and the reaction was stirred for an additional 1 h with the solution temperature of 0 °C. The resulting suspension was warmed slowly to room temperature and then refluxed for 16 h. After cooling, water (100 mL) was added to quench the reaction and the organic layer was separated and washed by water, dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, hexane/DCM = 1:1) to afford the crude product. The conversion is nearly quantitative and based on ^{1}H NMR analysis; a mixture of 3-formylperylene **2a** and 1-formylperylene **2b** in the ratio of about **2a**:**2b** = 1:4 was obtained. Pure **2b** can be separated by column chromatography, but no pure **2a** could be obtained. ^{1}H NMR of **2b** (300 MHz, CDCl3): δ 10.30 (s, 1H), 9.16 (d, 1H, J = 4.2 Hz), 8.30 (m, 3H), 8.27(d, 1H, J = 7.4 Hz), 7.94 (d, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.73 (d, 1H, J = 8.1 Hz), 7.68 (t, 1H, J = 8.0 Hz), 7.52 (m, 2H). The purified mixture with **2a/2b** roughly in 1:1 ratio was subjected to the subsequent oxidative esterification reaction. To a solution of 4-ethyl-1-methyl-4*H*- [1, 2, 4] triazol-1-ium iodide (EMTI, 65 mg, 0.27 mmol, 15 mol %) in dry tetrahydrofuran (THF, 15 mL) and dry MeOH (15 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (304 µL, 1.96 mmol, 110 mol %) was added, and the solution was stirred for two

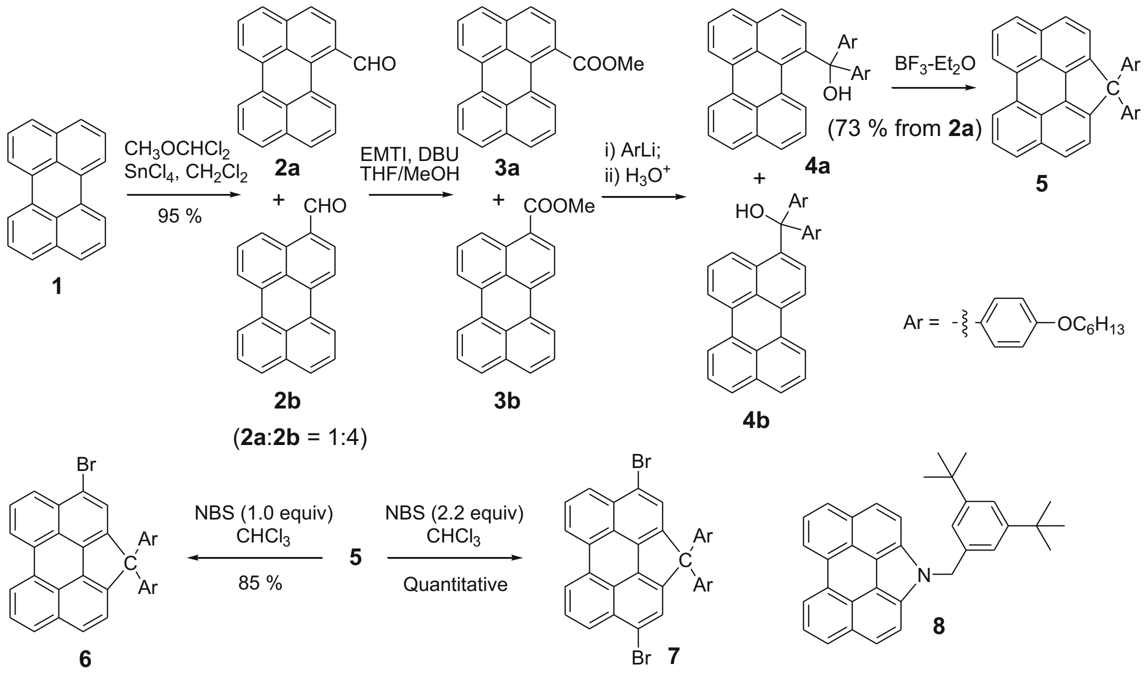

Fig. 2 Synthetic route of cyclopenta-fused perylenes **5**–**7**