Dyes and Pigments 95 (2012) 450–454

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Facile synthesis and replacement reactions of mono-substituted perylene bisimide dyes

Xiangxue Kong, Juan Gao, Tingting Ma, Ming Wang, Andong Zhang, Zhiqiang Shi*, Yanhong Wei

Department of Chemistry, Shandong Normal University, Jinan 250014, PR China

ARTICLE INFO

Article history:
Received 8 March 2012
Received in revised form
10 May 2012
Accepted 12 May 2012
Available online 19 May 2012

Keywords:
Dye
Perylene bisimide
Substitution reaction
Nitrification
Replacement reaction
Photophysical property

ABSTRACT

Mono-substituted perylene bisimides were synthesized in high yields under mild condition. The starting material was mono-nitrified perylene bisimides instead of usual perylene bisimides halogenated at different levels. Besides phenols and amine, the nucleophilic reagents included alcohol and thiol. The substitution of nitro group was easier and more effective than the substitution of halogen atoms. But the substitution reaction of pyrrolidine afforded mono- and 1,6-disubstituted perylene bisimides owing to the high activity of nitrified perylene bisimides and pyrrolidine. Several replacement reactions between phenols and alcohol based on phenol mono-substituted perylene bisimide were also found. The replacement reactions between phenols was fast and in high yield. The absorption of the mono-substituted perylene bisimides were tunable in the whole visible region.

1. Introduction

Perylene bisimides (PBIs) are important chromospheres in dye chemistry. In light of their diverse and fascinating properties, such as excellent electron acceptor ability, high molar extinction coefficient in the visible region, and high fluorescence quantum yields, PBI dyes represent a classical example of an inherently robust and outstandingly versatile family of organic compounds that have been extensively utilized for a wide range of high technology applications [1–14]. To meet the demands of various applications, the electrochemical and photophysical behavior need to be efficiently tuned by functionalization with hydrophobic, hydrophilic electron-donating or electron-withdrawing groups [15]. The general strategy for introducing groups onto the PBI core was substitution reactions or metal-catalyzed cross-coupling reactions using halogenated PBIs as starting materials. The chlorination or bromination of PBIs could be readily achieved but resulting in a mixture of various PBIs halogenated at different levels. The mixture usually couldn't be separated by column chromatography owing to the bad solubilities as well as the presence of regioisomers. The main products of replacement of the halogen atoms were di- or tetra- substituted symmetrical perylene derivatives [16–20]. Sometimes the mono-substituted derivatives need to be designed for special application. However, neither the halogenation nor the followed replacement of halogen atoms of PBIs was facile to be controlled at the first step [21,22]. In addition, the low activities of halogenated PBIs lead to some reactions are not easy to be carried out. While the nitrification of PBI can be readily controlled at the first step owing to the strong electron-withdrawing effect of nitro group. The mono-nitrated PBI can be achieved under ambient temperature in a high yield of 90%. However, the derivatization method of nitrified PBIs has seldom been investigated. Only a reduction reaction was reported recently to afford amino-substituted PBI [23]. Herein, a serious substitution reaction of mono-nitrified PBI were investigated using different nucleophilic reagents such as phenols, alcohol, thiol and amine. Several replacement reactions based on phenol mono-substituted perylene bisimide between phenols and alcohol were found.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality. All reagents were obtained from Sinopharm Chemical Reagent Co. Ltd used as received. All organic solvents employed were obtained from Beijing Chemical Corporation. Thin-layer chromatography (TLC) was done on aluminum sheets precoated with Silica 60 F254.

* Corresponding author. Tel.: +86 531 86182540; fax: +86 531 82615258.
E-mail address: zshi@sdnu.edu.cn (Z. Shi).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.05.009

The purification and isolation of the products were performed by column chromatography on silica gel 60, mesh size 40–63 μm or silica gel 100, mesh size 63–200 μm. *N,N′*-dicyclohexyl-3,4:9,10-tetracarboxylic acid bisimide **1** and *N,N′*-dicyclohexyl-1-nitroperylene-3,4:9,10-tetracarboxylic acid bisimide **2** were synthesized according to the literature procedure [24,25].

2.2. Equipment

^{1}H NMR and ^{13}C NMR were recorded on Bruker 300 MHz or 600 MHz spectrometers in $CDCl_3$ at room temperature. All chemical shifts are quoted relative to TMS ($\delta = 0.0$ ppm); δ values are given in ppm and *J* values in Hz. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. Electronic absorption spectra were measured on a Beijing Purkinje General Instrument Co. Ltd. TU-190 spectrophotometer. The photoluminescence spectra were recorded on a HITACHI FL-4500 spectrofluorometer.

2.3. Synthesis

2.3.1. Synthesis of *N,N′*-dicyclohexyl-1-(4-tert-butylphenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide (**3**)

Method a: Compound **2** (200 mg, 0.33 mmol), 4-*tert*-butylphenol (250 mg, 1.67 mmol), 300 mg K_2CO_3 and the catalyzed KI were suspended in 15 mL anhydrous NMP. The reaction mixture was stirred for 6 h at 25 °C under argon atmosphere. Then MeOH (10 mL) and 10% HCl solution (50 mL) were added into the reaction mixture. The precipitate was collected by filtration, washed with methanol, and then dried in vacuum. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a dark red solid (210 mg, 90%). Method b: A mixture of *N,N′*-dicyclohexyl-1-(4-formoxylphenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide **4** (50 mg, 0.074 mmol) and 4-*tert*-butylphenol (56 mg, 0.37 mmol) in 6 mL anhydrous NMP was stirred for 2 h at 50 °C under argon atmosphere. After being cooled to room temperature, MeOH (10 mL) and water (50 mL) was added into the reaction mixture. The precipitate was collected by filtration, washed with methanol, and then dried in vacuum. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give **3** (47 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): $\delta = 9.49$ (d, 1H, $J = 8.4$ Hz), 8.60 (m, 5H), 8.24 (s, 1H), 7.48 (d, 2H, $J = 7.8$ Hz), 7.10 (d, 2H, $J = 7.8$ Hz), 5.03 (m, 2H), 2.54 (m, 4H), 1.90 (m, 4H), 1.77 (m, 6H), 1.59–1.46 (m, 6H), 1.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta =$ 163.48, 163.30, 162.76, 156.06, 151.83, 148.54, 133.38, 133.30, 132.91, 132.13, 131.28, 130.51, 129.89, 128.87, 128.36, 127.94, 127.71, 127.49, 125.98, 124.89, 124.62, 124.08, 123.46, 123.32, 123.01, 124.31, 123.37, 123.21, 123.12, 122.81, 122.55, 122.03, 121.52, 119.34, 54.58, 54.21, 54.02, 34.55, 31.43, 29.09, 26.59, 25.50. MS (MALDI-TOF): $m/z = 702.33$ (M^+).

2.3.2. Synthesis of *N,N′*-dicyclohexyl-1-(4-formaldehyde phenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisimide (**4**)

Compound **4** was synthesized as the procedure of synthesis of **3**. 100 mg compound **2** and 100 mg 4-hydroxy-benzaldehyde reacted for 6 h in NMP to yield **4** in 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 9.99$ (s, 1H), 9.34 (d, 2H, $J = 8.3$ Hz), 8.67 (m, 4H), 8.57 (d, 2H, $J = 8.3$ Hz), 8.27 (s, 1H), 7.96 (d, 2H, $J = 8.6$ Hz), 7.20 (d, 2H, $J = 8.6$ Hz), 5.02 (m, 2H), 2.53 (m, 4H), 1.92 (m, 4H), 1.55–1.28 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta =$ 190.39, 163.64, 163.63, 162.88, 160.11, 153.78, 132.22, 131.84, 128.69, 126.03, 122.71, 118.81, 110.02, 54.01, 53.43, 29.10, 29.07, 26.52, 26.48, 25.42, 25.39. MS (MALDI-TOF): $m/z = 674.24$ (M^+).

2.3.3. Synthesis of 1-ethoxyl-*N,N′*-dicyclohexyl perylene-3,4:9, 10-tetracarboxylic diimide (**5**)

Method a: Compound **2** (100 mg, 0.17 mmol) and 100 mg K_2CO_3 were suspended in 6 mL chloroform and 4 mL ethanol. The mixture was refluxed for 10 h under argon atmosphere. After being cooled to room temperature, the solution was filtrated and evaporated to dryness. The crude product was purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a red solid **5** (45 mg, 45%). Method b: A mixture of compound **3** (100 mg, 0.14 mmol) and 100 mg K_2CO_3 in 4 mL chloroform and 4 mL ethanol was refluxed for 24 h under argon atmosphere. The solvent was evaporated under reduced pressure to give a solid residue. The crude product was washed with MeOH and then purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether 4:1 as the eluent to afford **5** (28 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 9.45$ (d, 2H, $J = 8.2$ Hz), 8.63–8.16 (m, 6H), 5.04 (m, 2H), 4.51 (m, 2H), 2.59 (m, 5H), 1.94–1.49 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta =$ 164.43, 163.65, 162.96, 132.33, 130.83, 130.04, 127.63, 126.14, 125.37, 124.41, 124.66, 54.79, 54.23, 53.98, 29.11, 26.52, 25.36. MS (MALDI-TOF): $m/z = 598.25$ (M^+).

2.3.4. Synthesis of 1-propylthio-*N,N′*-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**6**)

Compound **2** (100 mg, 0.17 mmol) and 100 mg K_2CO_3 were suspended in 6 mL chloroform and 4 mL n-propyl mercaptan. The mixture was refluxed for 10 h under argon atmosphere. After being cooled to room temperature, the solution was filtrated and evaporated to dryness. The crude product was further purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 4:1 to give a red solid **6** (37 mg, 35%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.82$ (d, 2H, $J = 8.0$ Hz), 8.65–8.60 (m, 3H), 8.55–8.46 (m, 3H), 5.05 (m, 2H), 3.20–3.15 (m, 2H), 2.61–2.57 (m, 5H), 1.96–1.93 (m, 4H), 1.83–1.75 (m, 6H), 1.52–1.38 (m, 8H), 1.09–1.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta =$ 163.59, 163.54, 163.43, 139.52, 133.72, 133.41, 132.82, 131.98, 131.03, 130.41, 130.26, 129.21, 128.88, 128.42, 127.29, 126.52, 125.99, 123.19, 123.07, 122.75, 122.02, 121.95, 54.19, 54.03, 37.95, 30.84, 29.15, 26.58, 25.48, 21.92, 13.54. MS (MALDI-TOF): $m/z = 628.24$ (M^+).

2.3.5. Synthesis of 1-pyrrolidinyl-*N,N′*-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**7a**) and 1,6-dipyrrolidinyl-*N,N′*-dicyclohexyl perylene-3,4:9,10-tetracarboxylic diimide (**7b**)

Compound **2** (100 mg, 0.17 mmol) in 5 mL pyrrolidine was stirred at 0 °C for 5 h under argon atmosphere. After the solvent being evaporated, the solid was purified by silica gel column chromatography with the eluent CH_2Cl_2/petroleum ether 2:1 to give blue solid **7**a (32 mg, 30%) and blue-green solid **7**b (24 mg, 20%). **7**a: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.64$ (d, 2H, $J = 8.0$ Hz), 8.47–8.52 (m, 4H), 7.53 (d, 2H, $J = 8.0$ Hz), 5.09 (m, 2H), 3.79 (m, 2H), 2.79 (m, 2H), 2.65–2.57 (m, 4H), 2.13 (m, 2H), 1.96–1.92 (m, 4H), 1.81–1.78 (m, 6H), 1.52–1.38 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta =$ 164.31, 164.24, 164.13, 148.42, 135.19, 134.93, 132.51, 130.90, 130.65, 128.94, 127.07, 126.58, 124.18, 123.57, 123.11, 122.83, 122.57, 122.14, 120.38, 119.53, 115.96, 53.99, 53.75, 52.24, 29.68, 29.18, 29.10, 26.60, 25.72, 25.50. MS (MALDI-TOF): $m/z = 623.28$ (M^+). **7**b: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 8.65$ (d, 2H, $J = 8.0$ Hz), 8.33 (s, 2H), 7.90 (d, 2H, $J = 8.0$ Hz), 5.13–5.04 (m, 2H), 3.71 (m, 4H), 2.67–2.56 (m, 8H), 2.01–1.90 (m, 12H), 1.76 (m, 6H), 1.27–1.51 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta =$ 160.10, 159.85, 145.27, 130.76, 126.26, 125.40, 123.70, 123.55, 118.60, 118.56, 113.62, 112.85, 112.46, 112.22, 49.20, 48.80, 47.30, 24.48, 24.38, 21.89, 21.83, 20.87. MS (MALDI-TOF): $m/z = 692.34$ (M+).