# Synthesis and optical properties of novel asymmetric perylene bisimides

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## ARTICLE INFO

## ABSTRACT

A novel series of asymmetric perylene bisimides, 1-amino-7-nitroperylene bisimides (**1a**–**1c**), was synthesized and fully characterized. These molecules undergo an excited-state intramolecular electron transfer reaction, resulting in a unique charge transfer emission in the near-infrared region, of which the peak wavelength exhibits strong solvatochromism. The dipole moments of these compounds have been estimated using the Lippert–Mataga equation, and upon excitation, the molecules show larger dipole moment changes than those of the symmetric 1,7-diaminoperylene bisimides (**2a**–**2c**). Furthermore, these dyes undergo two quasi-reversible one-electron oxidations and two quasi-reversible one-electron reductions in dichloromethane at modest potentials. They display good thermal stability and optical stability that can be used as stable near-infrared fluorescent dyes. Their spectroscopic properties in various conditions and complementary time-dependent density functional theory calculations are reported.

## 1. Introduction

Perylene bisimides (PBIs) and their related derivatives have attracted considerable attention due to their potential applications in molecular electronic and optical devices, such as dye lasers [1], optical power limiters [2], light-emitting diodes [3,4], organic field-effect transistors (OFETs) [5–10], light-harvesting arrays [11,12], photovoltaic cells [13–22], LCD color filters [23,24], electrophotographic devices [25], photochromic materials [26,27], logic gates [28] and molecular wires [29,30]. PBIs have also been utilized as building blocks to construct supramolecular or artificial photosynthetic systems [31–33]. These molecules are advantageous due to their high photochemical and optical stabilities, ease of synthetic modification and reversible redox properties [34–40]. Furthermore, the electronic characteristics of PBIs can be fine-tuned by the substitution of the conjugated aromatic core. Many perylene bisimide derivatives with either electron-donating or electron-withdrawing groups have been extensively reported on over the past two decades, including: (a) piperidinyl-substituted PBIs [41–43], (b) pyrrolidinyl-substituted PBIs [44–46], (c) alkylamino-substituted PBIs [47–49], (d) amino-substituted PBIs [50,51], (e) alkoxy-substituted PBIs [52–56], (f) hydroxy-substituted PBIs [57,58], (g) aryl-substituted PBIs [59,60], (h) ferrocenyl-substituted PBIs [61,62], (i) alkyl-substituted PBIs [63], (j) perfluoroalkyl-substituted PBIs [64,65], (k) boryl-substituted PBIs [66], (l) cyano-substituted PBIs [67,68], (m) nitro-substituted PBIs [69–71], etc. To date, a principal method for introducing substituents

onto the PBIs core is bromination or chlorination of perylene dianhydride. Subsequently, nucleophilic substitutions and metal-catalyzed cross-coupling reactions can be executed [41–49]. The most common products made from the above reaction were disubstituted (1,7- and 1,6-) symmetric PBIs, rather than asymmetric PBIs [72–74]. Sometimes the asymmetric PBIs need to be designed for special applications [75,76]. In an effort to expand the scope of the PBI-based chromophores available for designing systems for organic optoelectronic materials and fluorescent dyes, the present research reports the synthesis of a novel series of asymmetric PBIs, as well as their optical and electrochemical properties, and complementary time-dependent density functional theory (TD-DFT) calculations.

## 2. Experimental

### 2.1. Chemicals and instruments

The starting materials such as perylene-3,4,9,10-tetracarboxyldianhydride, cyclohexylamine, butylamine, octylamine, acetic acid, cerium (IV) ammonium nitrate (CAN), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF) and tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) were purchased from Merk, ACROS and Sigma-Aldrich. Solvents were distilled freshly according to standard procedure. Column chromatography was performed using silica gel Merk Kieselgel *si* 60 (40–63 mesh).

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 MHz. Mass spectra were recorded on a VG70-250S mass spectrometer. The absorption and emission spectra were measured using a Jasco

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V-570 UV–vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) was performed with a CH instruments at a potential rate of 200 mV/s in a 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane. Platinum and $Ag/AgNO_3$ electrodes were used as counter and reference electrodes, respectively. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10 °C/min with a TA Instruments Thermogravimetric Analyzer 2050. DSC measurements were performed using a Perkin-Elmer DSC-7 calorimeter at a heating rate of 10 °C/min under a nitrogen atmosphere.

## 2.2. Synthesis and characterization

### 2.2.1. Synthesis of 1,7-dinitroperylene bisimides (4a–4c)

**6a** (**6b** or **6c**) (1.8 mmol), cerium (IV) ammonium nitrate (CAN) (4.8 g, 8.8 mmol), nitric acid (8.0 g, 131.1 mmol) and dichloromethane (250 ml) were stirred at 25 °C under $N_2$ for 48 h. The mixture was neutralized with 10% KOH and extracted with $CH_2Cl_2$. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent $CH_2Cl_2$ to afford a mixture of 1,7- and -1,6-dinitroperylene bisimides, and $^1H$ NMR (400 MHz) analysis revealed a 3:1 ratio. The regioisomeric 1,7- and 1,6-dinitroperylene bisimides could not be separated by column chromatography. Regioisomerically pure 1,7-dinitroperylene bisimides (**4a–4c**) were obtained by repeated crystallizations. Characterization data: **4a**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.67 (d, J=8.4 Hz, 2H), 8.28 (d, J=8.4 Hz, 2H), 4.99 (m, 2H), 2.51 (m, 4H), 1.92 (m, 4H), 1.74 (m, 6H), 1.46 (m, 4H), 1.36 (m, 2H); MS (FAB): m/z (relative intensity) 645 (M+H$^+$, 100); HRMS calcd. for $C_{36}H_{29}O_8N_4$ 645.1985, found 645.1981. Selected data for **4b**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 2H), 8.71 (d, J=8.0 Hz, 2H), 8.30 (d, J=8.0 Hz, 2H), 4.20 (m, 4H), 1.75 (m, 4H), 1.26–1.53 (m, 20H), 0.87 (t, J=6.4 Hz, 6H); MS (FAB): m/z (relative intensity) 705 (M+H$^+$, 100); HRMS calcd. for $C_{40}H_{41}O_8N_4$ 705.2924, found 705.2923. Selected data for **4c**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 2H), 8.63 (d, J=8.0 Hz, 2H), 8.26 (d, J=8.0 Hz, 2H), 4.18 (m, 4H), 1.74 (m, 4H), 1.47 (m, 4H), 0.96 (t, J=6.0 Hz, 6H); MS (FAB): m/z (relative intensity) 593 (M+H$^+$, 100); HRMS calcd. for $C_{32}H_{25}O_8N_4$ 593.1672, found 593.1674.

### 2.2.2. Synthesis of 1,7-diaminoperylene bisimides (2a–2c)

Tin chloride dihydrate (1.0 g, 4.8 mmol), and **4a** (**4b** or **4c**) (0.5 g, 0.8 mmol) were suspended in 50 ml of THF, and stirred at 25 °C under $N_2$ for 20 min. The solvent was refluxed 80 °C with stirring for 6 h. THF is removed at the rotary evaporator, and the residue was dissolved in ethyl acetate and washed with 10% sodium hydrate solution and brine. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/n-hexane (4/5) to afford **2a** (**2b** or **2c**) in 82% yield. Characterization data: **2a**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J=8.4 Hz, 2H), 8.43 (d, J=8.4 Hz, 2H), 8.14 (s, 2H), 5.04, (m, 2H), 4.94 (s, 4H), 2.61 (m, 4H), 1.93 (m, 4H), 1.74 (m, 6H), 1.36–1.54 (m, 6H); MS (FAB): m/z (relative intensity) 585 (M+H$^+$, 100); HRMS calcd. for $C_{36}H_{33}O_4N_4$ 585.2502, found 585.2504. Selected data for **2b**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J=8.4 Hz, 2H), 8.46 (d, J=8.4 Hz, 2H), 8.17 (s, 2H), 4.96, (s, 4H), 4.19 (m, 4H), 1.75 (m, 4H), 1.26–1.53 (m, 20H), 0.87 (t, J=6.4 Hz, 6H); MS (FAB): m/z (relative intensity) 645 (M+H$^+$, 100); HRMS calcd. for $C_{40}H_{45}O_4N_4$ 645.3441, found 645.3447. Selected data for **2c**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J=8.0 Hz, 2H), 8.40 (d, J=8.0 Hz, 2H), 8.10 (s, 2H), 4.92, (s, 4H), 4.19 (m, 4H), 1.76 (m, 4H), 1.48 (m, 4H), 0.90 (t, J=6.0 Hz, 6H); MS (FAB): m/z (relative intensity) 533 (M+H$^+$, 100); HRMS calcd. for $C_{32}H_{29}O_4N_4$ 533.2189, found 533.2185.

### 2.2.3. Synthesis of 1-amino-7-nitroperylene bisimides (1a–1c)

Tin chloride dihydrate (0.6 g, 3.6 mmol), and **4a** (**4b** or **4c**) (0.4 g, 0.6 mmol) were suspended in 50 ml of THF, and stirred at 25 °C under $N_2$ for 20 min. The solvent was refluxed 80 °C with stirring for 1 h. THF is removed at the rotary evaporator, and the residue was dissolved in ethyl acetate and washed with 10% sodium hydrate solution and brine. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/n-hexane (2/3) to afford **1a** (**1b** or **1c**) in 60%. Characterization data: **1a**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J=8.0 Hz, 1H), 8.81 (s, 1H), 8.73 (d, J=8.4 Hz, 1H), 8.39 (d, J=8.0 Hz, 1H), 8.16 (s, 1H), 8.15 (d, J=8.4 Hz, 1H), 5.33, (s, 2H), 5.07 (m, 2H), 2.55 (m, 4H), 1.94 (m, 4H), 1.77 (m, 6H), 1.36–1.54 (m, 6H); MS (FAB): m/z (relative intensity) 615 (M+H$^+$, 100); HRMS calcd. for $C_{36}H_{31}O_6N_4$ 615.2244, found 615.2240. Selected data for **1b**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J=8.0 Hz, 1H), 8.84 (s, 1H), 8.76 (d, J=8.4 Hz, 1H), 8.41 (d, J=8.4 Hz, 1H), 8.19 (s, 1H), 8.15 (d, J=8.0 Hz, 1H), 5.38, (s, 2H), 4.19 (m, 4H), 1.77 (m, 4H), 1.24–1.43 (m, 20H), 0.88 (t, J=6.4 Hz, 6H); MS (FAB): m/z (relative intensity) 675 (M+H$^+$, 100); HRMS calcd. for $C_{40}H_{43}O_6N_4$ 675.3183, found 675.3189. Selected data for **1c**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J=8.0 Hz, 1H), 8.86 (s, 1H), 8.77 (d, J=8.0 Hz, 1H), 8.42 (d, J=8.0 Hz, 1H), 8.20 (s, 1H), 8.17 (d, J=8.0 Hz, 1H), 5.37 (s, 2H), 4.21 (m, 4H), 1.77 (m, 4H), 1.46 (m, 4H), 0.92 (t, J=6.0 Hz, 6H); MS (FAB): m/z (relative intensity) 563 (M+H$^+$, 100); HRMS calcd. for $C_{32}H_{27}O_6N_4$ 563.1931, found 563.1936.

## 2.3. Computational methods

The Gaussian 03 program was used to perform the ab initio calculation on the molecular structure [77]. Geometry optimizations for compounds **1–3** were carried out with the 6-31G$^{**}$ basis set to the B3LYP functional. Vibrational frequencies were also performed to check whether the optimized geometrical structures for all compounds were at energy minima, transition states, or higher order saddle points. After obtaining the converged geometries, the TD-B3LYP/6-31G$^{**}$ was used to calculate the vertical excitation energies. Emission energies were obtained from TDDFT/B3LYP/6-31G$^{**}$ calculations performed on $S_1$ optimized geometries.

## 3. Results and discussion

### 3.1. Synthesis of dyes

The chemical structures of symmetric (**2a–2c**) and asymmetric PBIs (**1a–1c** and **3a–3c**) and their synthetic routes are shown in Scheme 1. The synthesis starts from an imidization of perylene dianhydride (**7**) by reaction with cyclohexylamine, octylamine or butylamine. The dinitration of PBIs (**6a–6c**) can then be achieved by the reaction of PBIs with cerium (IV) ammonium nitrate (CAN) and $HNO_3$ under ambient temperature for 48 h, giving dinitroperylene bisimides in high yields of ca. 90%. Among the products, a 3:1 mixture of isomers (nitrated at the 1,7- or 1,6-positions) was indicated by $^1H$ NMR spectroscopy [69]. Pure 1,7-regioisomer (**4a–4c**) are obtained through repetitive crystallizations. Careful control of the reaction time allows mono- and direduction of **4a–4c** to produce asymmetric 1-amino-7-nitroperylene bisimides (**1a–1c**) and symmetric 1,7-diaminoperylene bisimides (**2a–2c**), respectively. The asymmetric structures of 1-amino-7-nitroperylene bisimides (**1a–1c**) can be verified by the presence of six signals (two singlet and four doublet signals) at δ 8.0–9.0 ppm in the $^1H$ NMR spectrum, which indicates that there are six different kinds of protons in the perylene