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Regioisomerically Pure 1,7-Dibromo-Substituted Perylene Bisimide Dyes: Efficient Synthesis, Separation, and Characterization

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1,7-Dibromo-substituted perylene bisimides have been obtained in yields of at least 60 % in regioisomerically pure form by treating the commonly used dibromoperylene-3,4,9,10-tetracarboxylic dianhydride with 2-(diethylamino)ethylamine or 2-(dimethylamino)ethylamine and then separating the 1,7-isomer from the regioisomeric mixtures by conventional column chromatography and without recrystallization. The individual regioisomers were fully characterized by ^{1}H NMR spectroscopy and HRMS. The signals of the protons located in the aromatic region and neighboring the imide nitrogen atom were utilized to confirm the chemical structures of the isomers. The 1,7-dibromo isomer obtained with 2-(dimethylamino)ethylamine in such a convenient and efficient way was further used to prepare 1,7-disubstituted perylene bisimide derivatives by saponification, amidation, and then bay-position substitution reactions. These compounds exhibited a significant redshift and broadening of their absorption and emission in optical spectroscopy analysis.

Introduction

Perylene bisimides (PBIs) have been extensively utilized for a wide range of high technology applications owing to their outstanding properties such as intense absorption in the visible region, high fluorescence quantum yield, strong electron-accepting character, and excellent photochemical stability.[1] One of the crucial characteristics of PBIs, which greatly enhances their utility in comparison with other organic dyes, is the possibility of fine-tuning their molecular-level electronic and optical properties.[2] The last decade has witnessed their extensive utilization in numerous electronic and optical applications,[3] for example, in organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic solar cells, photosensitizers, fluorescent sensors, and molecular wires.

PBIs can be structurally modified either at the "*peri*" (carboxylic acid) position or in the "bay" region (1-, 6-, 7-, and 12-positions) by the attachment of various electron-donor or electron-acceptor groups.[2,4] In accord with the requirement of various applications, numerous functionalized PBIs with interesting optical and electrochemical properties have been synthesized by modification of the bay region. The strategy of bay substitution generates certain other key advantages simultaneously. For example, it can clearly improve the solubility of such derivatives in water or organic solvents by reducing π–π stacking and also provides extra sites, in addition to the *peri* positions, for the attachment of other functional groups.[3d,3e,5] Therefore the bay-functionalization approach is crucial for controlling the chemical structures and physical properties of PBIs. The most widely used procedure for the preparation of bay-functionalized PBIs involves the use of dibromoperylene bisimide as the intermediate due to the facile exchange of the bromo substituents in the bay region with various nucleophiles.[2a,4] However, dibromination products of perylene-3,4,9,10-tetracarboxylic dianhydride are obtained as mixtures of 1,7- and 1,6-isomers and so subsequent imidization produces isomerically impure bay-substituted compounds.[6] In an alternative approach, dibromoperylene bisimides have been prepared by the direct bromination of non-bay-substituted PBIs.[7] However, regioisomeric mixtures are also obtained in this case. It has been demonstrated recently that the optical and electrochemical properties of 1,6- and 1,7-substituted PBIs can be markedly different.[6,8] Therefore the isomeric purity of these compounds is highly relevant.

Imidization of dibromoperylene-3,4,9,10-tetracarboxylic dianhydride with cyclohexylamine yielded a regioisomeric mixture of 1,7- and 1,6-dibromoperylene bisimides, which were successfully separated by using a repetitive and slow recrystallization process.[9] Tetrabutyl 1,7-dibromoperylene-3,4,9,10-tetracarboxylate has also been obtained in regioisomerically pure form by employing a recrystallization method in which the regioisomeric tetrabutyl 1,7- and 1,6-dibromoperylene-3,4,9,10-tetracarboxylates were synthesized from commercially available 3,4,9,10-perylenetetracarboxylic dianhydride and then the desired 1,7-isomer was

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obtained in pure form by crystallization from an acetonitrile/dichloromethane mixture.[10] Recrystallization is the only existing method for obtaining regioisomerically pure 1,7-dibromoperylene bisimide. However, the method is generally not suitable for the fast synthesis of regioisomerically pure derivatives because it is inefficient and cumbersome.

We present herein the very first synthesis of regioisomerically pure 1,7-dibromoperylene bisimides by the reaction between dibromoperylene-3,4,9,10-tetracarboxylic dianhydride and 2-(diethylamino)- or 2-(dimethylamino)ethylamine. The reported reaction is suitable for the efficient synthesis of various isomerically pure 1,7-dibromoperylene derivatives because of their satisfactory yields and convenient purification.

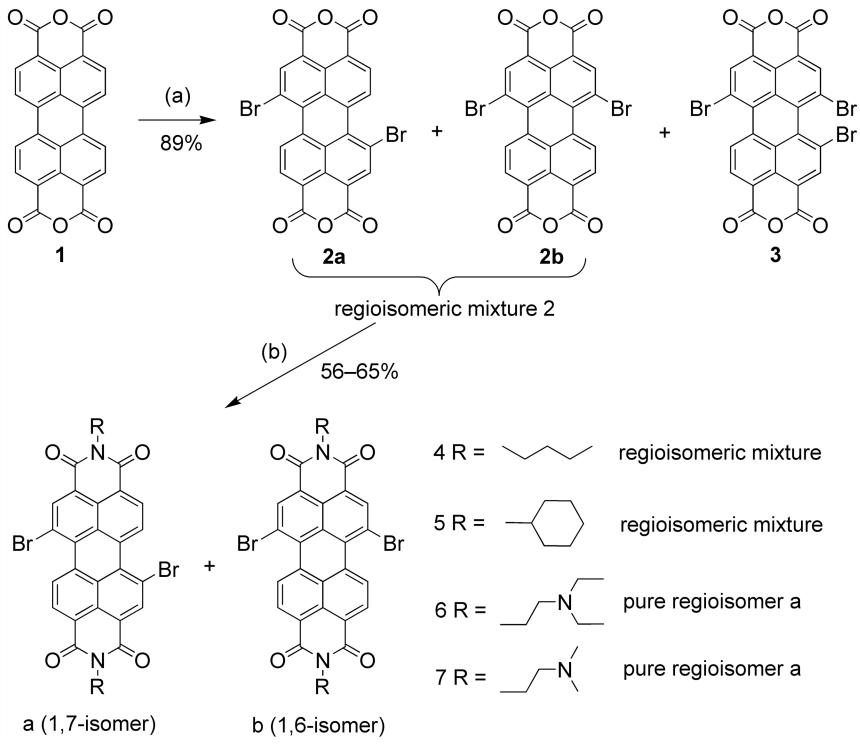
Results and Discussion

Synthesis, Separation, and Characterization

As shown in Scheme 1, the synthesis of compounds **2**–**7** began with commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (**1**). All of the compounds were prepared in two steps from **1** in overall yields of between 56 and 89%.

In the first step, dibromoperylene-3,4,9,10-tetracarboxylic dianhydride was synthesized.[11] This crude product mixture contained a mixture of 1,7- and 1,6-dibromoperylene dianhydrides **2a** and **2b** along with 1,6,7-tribromoperylene dianhydride **3**.[6a] Compounds **2a**, **2b**, and **3** could not be purified by general methods because of their insolubility in common organic solvents. Therefore the crude product mixture was used in the subsequent imidization reactions with primary amines (Scheme 1). Imidization of **2** with *n*-butylamine in the presence of acetic acid as catalyst and *N*-methylpyrrolidone (NMP) as solvent under reflux conditions yielded perylene bisimides **4**. The mixture was subjected to silica gel column chromatography with CH_2Cl_2 or other mixed organic solvents as eluent. However, **4a** could not be obtained in pure form, even after recrystallization from CH_2Cl_2/MeOH three times (see Figure S1 in the Supporting Information).

The 400 MHz ^{1}H NMR spectrum of crude **4** in Figure 1 (a) exhibits signals with different intensities in the aromatic region indicating the presence of 1,7- and 1,6-isomers in the product mixture. In accord with a previous report,[9] the relatively strong signals (two doublets and one singlet) were assigned to the protons of the 1,7-isomer. The dibromides **4** were obtained in a 2:1 molar ratio. We speculated that the polarity of the *peri* substituents might have an impact on the separation of the 1,7- and 1,6-isomers. Pure 1,7-isomer **5a** was also difficult to obtain by treatment of the mixture of **2** with cyclohexylamine (Scheme 1, b, Figure 1, b). Fortunately, the imidization of **2** with 2-(diethylamino)ethylamine with 2-propanol/H_2O as reaction solvent yielded pure 1,7-isomer **6a** by careful chromatography on a silica gel column with CH_2Cl_2/MeOH as eluent. *N*-Dimethylacetamide (DMA)/1,4-dioxane could be used instead of 2-propanol/H_2O as solvent,[12] but its use led to an inconvenient purification procedure due to the high boiling point of DMA. The ^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



Scheme 1. Synthesis of bromo-substituted perylene bisimides. Reagents and conditions: (a) bromine, I_2/H_2SO_4, 85 °C, 24 h; (b) *n*-butylamine, acetic acid/NMP, 85 °C, 12 h for **4**, cyclohexylamine, acetic acid, NMP, 85 °C, 12 h for **5**, 2-(diethylamino)ethylamine, acetic acid, 2-propanol/H_2O, 80 °C, 24 h for **6**, 2-(dimethylamino)ethylamine, acetic acid, 2-propanol/H_2O, 80 °C, 18 h for **7**.

in Figure 1 (c) shows the absence of the 1,6-isomer. The introduction of diethyl tertiary amine groups at the *peri* positions changed the polarity of the 1,6-isomer and improved the efficiency of the regioisomer separation.

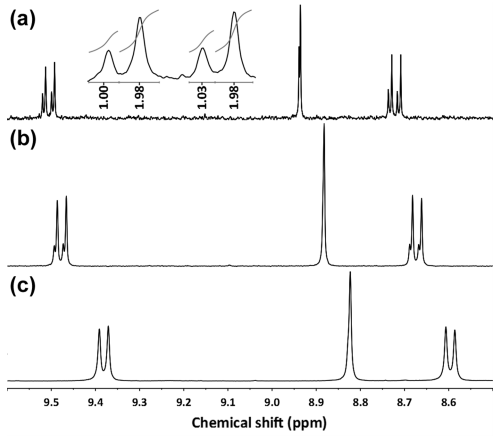


Figure 1. ^{1}H NMR spectra of **4** (a), **5** (b), and **6a** (c) in the aromatic region.

To verify the function of the diethyl tertiary amine groups in the separation of regioisomerically pure 1,7-dibromo-substituted PBIs, **7a** was prepared by treating **2** with 2-(dimethylamino)ethylamine. Pure **7a** could also be obtained by column chromatography. In fact, the 1,7- (**7a**) and 1,6-isomers (**7b**) existed together in the initial product mixture prior to purification, which was also proved by ^{1}H NMR spectroscopy (see Figure S2 in the Supporting Information). Figure 2 (a) shows the signals of protons attributed to **7a** in the aromatic region, and are the same as for **6a** (Figure 1, c). In addition, the multiplet signal at around 4.3 ppm (Figure 2, b and c for **6a** and **7a**, respectively) has been assigned to the protons neighboring the imide nitrogen atom. For the 1,7-isomer, the signal was a single multiplet,[6a] whereas it has been reported that the 1,6-isomer signal shows two multiplets.[13] This confirms that the compound isolated was the 1,7-isomer.

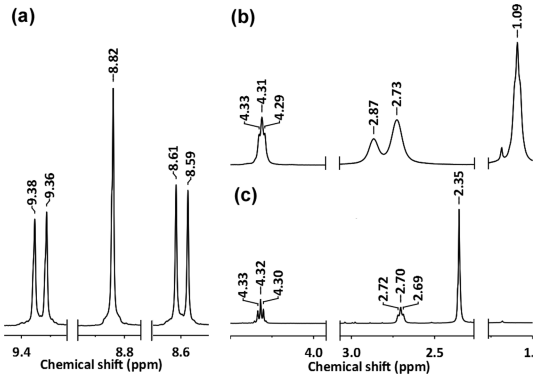
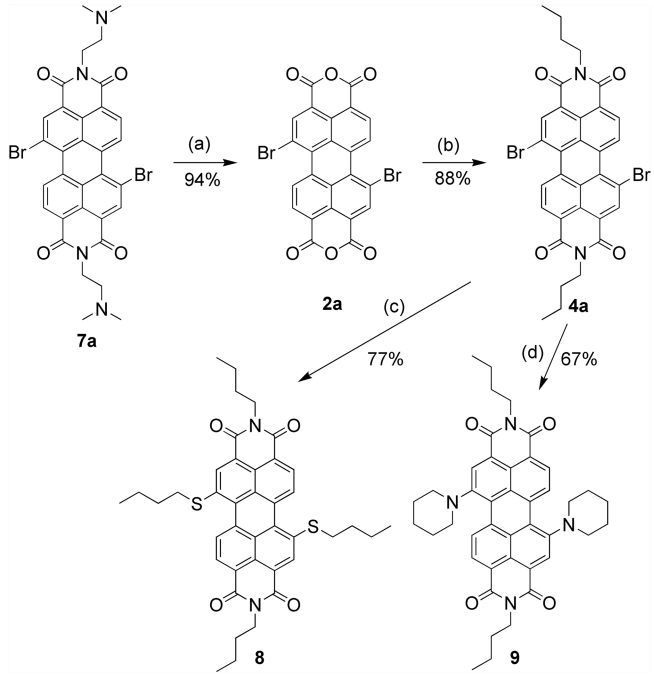


Figure 2. ^{1}H NMR spectra of **7a** (a) in the aromatic region and **6a** (b) and **7a** (c) in the high-field region.

Typically, **7a** was prepared on a 1.9 g scale, and 1.5 g of the pure 1,7-isomer was obtained. The treatment of **7a** with an excess of KOH in 2-propanol afforded 1,7-dibromo-substituted perylene dianhydride **2a** in 94% yield (Scheme 2). The bromine substituents in the bay region were hydrolyzed only slightly, even though dihydroxyperylene bisimides can be synthesized by nucleophilic substitution of brominated perylene bisimides.[14] Compound **2a** is a valuable and highly versatile synthon that provides direct access to many perylene derivatives. Compared with the well-established methods developed for the bromination of perylene dianhydride, **7a** could be saponified without the generation of the 1,6-isomer and 1,6,7-tribromide as an inseparable mixture. Therefore this reaction is a simple and efficient method for obtaining isomerically pure **2a**. Owing to the low solubility of **2a**, subsequent imidization with *n*-butylamine was directly carried out to yield pure 1,7-dibromo-substituted perylene bisimide **4a**. The chemical structure was confirmed by ^{1}H NMR spectra (Figure 3, a).



Scheme 2. Synthesis of 1,7-disubstituted perylene bisimides. Reagents and conditions: (a) KOH/2-propanol, 80 °C, 12 h; (b) *n*-butylamine, acetic acid/NMP, 85 °C, 12 h; (c) *n*-butanethiol, K_2CO_3, CTAB, *o*-xylene, 80 °C, 12 h; (d) piperidine, 55 °C, 24 h.

Various methods, such as Suzuki and Sonogashira coupling reactions and nucleophilic aromatic substitution reactions, have been reported for attaching functional substituents to 1,7-dibromo-PBIs such as **4a**.[11,15] We demonstrated that **4a** as a synthon could be used for bay-position substitution and the corresponding regioisomerically pure 1,7-isomers **8** and **9** were synthesized by alkanethiol and piperidine coupling, respectively.

Owing to the stronger nucleophilicity of alkylthio groups compared with alkoxy groups, the reaction between **4a** and *n*-butanethiol occurred much more easily and gave the bis-(alkylthio)-substituted PBI **8** as the main product. As displayed in Scheme 2, this reaction occurred in a phase-transfer (PT) system with *o*-xylene as the solvent, potassium carbonate as the base, and cetyltrimethylammonium brom-

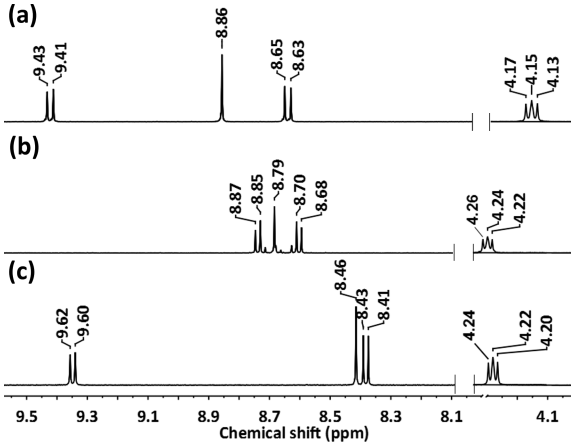


Figure 3. ^{1}H NMR spectra of **4a** (a), **8** (b), and **9** (c).

ide (CTAB) as the PT catalyst. The reaction proceeded smoothly at 80 °C to aord **8** in 77% yield. This is comparable to the method used to prepare sulfhydryl-substituted PBIs.[16] Compound **9** has been reported elsewhere.[17] The reaction of **4a** with piperidine proceeded easily under mild reaction conditions and afforded **9** in 67% yield. Compounds **8** and **9** were readily separated by silica gel column chromatography.

The ^{1}H NMR spectra in Figure 3 show the typical signals of compounds **4a**, **8**, and **9**. In the aromatic area, separate signals (one doublet, one singlet, and one doublet in sequence) reveal the specific symmetry of the 1,7-isomers.[6a,18] The high-field shift, from 8.86 to 8.79 ppm for **8** and 8.86 to 8.46 ppm for **9**, respectively, has been attributed to the greater nucleophilicity of the bay-position substituents. In addition, the single multiplet signal at around 4.2 ppm has been assigned to the protons neighboring the imide nitrogen atom in the pure 1,7-isomers, as mentioned above, thereby confirming the isolation of regioisomerically pure 1,7-isomers.

Steady-State Absorption and Fluorescence

3,4,9,10-Perylenetetracarboxylic dianhydride (**1**) possesses a very narrow absorption band and is insoluble in most organic solvents. Compared with modification of the *peri* position, introduction of functional groups into the bay region of PBIs is more attractive as it not only modifies the electronic and optical properties, but also improves the solubility.[19] Substitution in the bay region always leads to a broadening of the absorption range of PBIs and helps to capture more photons for optical devices, and greater solubility improves its processability.[20] Recently, it has been shown that 1,7- and 1,6-bis(substituted) PBIs could display very different optical and electrochemical properties depending upon the electronic nature of the substituents.[6b,8a] Therefore it is worth noting that the pure 1,7-isomers obtained in this work are significant synthons for studying the relationship between the molecular structures and optical properties of PBIs.

The ground-state absorption spectra of compounds **4**, **5**, **6a**, and **7a** in CH_2Cl_2 are presented in Figure 4. In comparison with unsubstituted PBI,[21] the absorption spectra show a slight bathochromic shift. The absorption spectra of all these PBIs are dominated by characteristic π–π* transitions and are similar for **4**, **5**, **6a**, and **7a**. The absorption bands attributed to the $S_0 \rightarrow S_1$ electronic transition appear at around 530 nm in CH_2Cl_2 and the characteristic absorption in the range 375–450 nm belongs to the $S_0 \rightarrow S_2$ electronic transition.[22] In addition, the spectra in Figure 4 show that substituents in the *peri* position have no influence on the maximum absorption wavelength of dibromo-substituted PBIs.

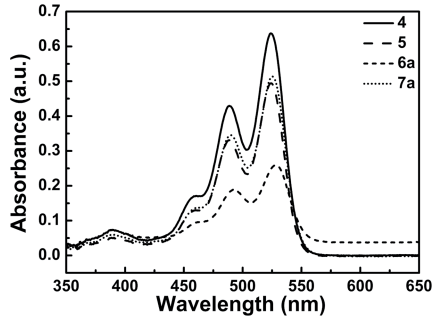


Figure 4. Ground-state absorption spectra of **4**, **5**, **6a**, and **7a** in CH_2Cl_2 (concentration: 10^{-5} μM).

In comparison with the dibromo-substituted PBIs, the absorption spectra of **8** and **9** show a significant bathochromic shift along with considerable band broadening (Figure 5). These results have been attributed to the pronounced electronic interaction between the PBI core and nucleophilic groups.[6a] In contrast, the negative inductive effect of bay-position substituents results in small redshift in their absorption spectra compared with other PBI derivatives.[13] Figure 5 (a) shows the redshift of the main absorption and emission wavelengths of **8** due to the incorporation of two electron-donating alkylthio groups. The ground-state absorption and fluorescence spectra of **9** (Figure 5, b) are the same as those reported in the literature.[17] It is also interesting to note that **8** and **9** show broad absorption spectra covering almost the whole visible spectrum with unusual dual absorption bands, with one peak at 430 nm and the other at 575 nm for **8**, and one peak at 430 nm and the other at 680 nm for **9**. The first peak can be attributed to

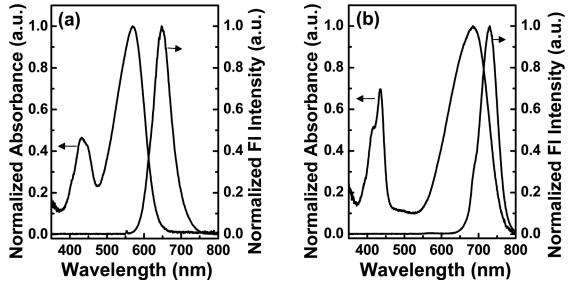


Figure 5. Steady-state absorption and emission spectra of **8** (a) and **9** (b) in CH_2Cl_2 (concentration: 10^{-5} μM).

charge-transfer electronic transitions from the electron-rich S–C and N–C units to the electron-deficient perylene core, whereas the second peak is usually a result of a π–π* transition. The above results underline the importance and value of **4a** as a synthon for the synthesis of pure 1,7-dibromoperylene bisimides.

Conclusions

The 1,7-regioisomer of dibromoperylene bisimides were obtained in regioisomerically pure form by a highly efficient and scalable synthesis starting from dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride and 2-(diethylamino)- or 2-(dimethylamino)ethylamine. These regioisomerically pure intermediates were successfully isolated from a regioisomeric mixture by using conventional silica gel column chromatography and characterized by ^{1}H NMR spectroscopy and HRMS. This method of separation of the regioisomers is a useful alternative as it does not involve prolonged repetitive recrystallization. The 1,7-dibromo isomer obtained with 2-(dimethylamino)ethylamine is of special interest as it provides access to symmetrical and unsymmetrical perylene bisimide derivatives by substitution of the 1,7-bromine atoms in the bay region. The pure 1,7-isomer was unambiguously identified by ^{1}H NMR spectroscopy by observing the chemical shifts of the four methylene protons next to the imide nitrogens in the *peri* positions and by the chemical shifts of the perylene core protons. All the synthesized PBI derivatives have been studied by optical spectroscopy, which showed broad absorption in the visible spectrum for the alkylthio and piperidinyl groups in the bay region. These findings could be useful for the conversion of solar energy into electricity.

Experimental Section

Materials and Characterization: 3,4,9,10-Perylenetetracarboxylic dianhydride, 2-(diethylamino)ethylamine, 2-(dimethylamino)ethylamine, and piperidine were purchased from Energy Chemical (China). *N*-Methylpyrrolidone (NMP), *n*-butylamine, *n*-butanethiol, and other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents and solvents were of analytical or chemical grade and were purified by using standard methods. ^{1}H NMR spectra were recorded with a Bruker DPX 300 spectrometer (400 MHz) using $SiMe_4$ as reference. Mass spectra were recorded with a Bruker BIFLEX III mass spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix. Stock solutions of the PBIs (10^{-3} M) were prepared in CH_2Cl_2. UV/Vis absorption spectra were recorded with a Shimadzu UV-2550 PC spectrophotometer. Fluorescence spectra were obtained with a Shimadzu RF-5301PC spectrofluorimeter.

Synthesis of Dibromoperylene-3,4,9,10-tetracarboxylic Dianhydride (2): 3,4,9,10-Perylenetetracarboxylic dianhydride (5.70 g, 14.5 mmol) was added to concentrated sulfuric acid (80 mL) and the mixture stirred at 55 °C for 24 h. Iodine (137 mg, 0.54 mmol) was added to the reaction mixture and stirred for an additional 5 h at 55 °C. Bromine (1.6 mL, 32 mmol) was added dropwise to the reaction flask over 30 min and then stirred for 24 h at 85 °C. After cooling to room temperature, the excess bromine was eliminated by bubbling air into the reaction mixture. The reaction product was precipitated by slow addition of ice–water (40 mL). After filtration and washing with water until the mixture was pH neutral, the solid was dried at 120 °C in vacuo. The crude product (**2** and **3**, 10 g, 89%, containing 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride, 1,6-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride, and 1,6,12-tribromoperylene-3,4,9,10-tetracarboxylic dianhydride) could not be purified owing to its insolubility in organic solvents.

Dibromo-*N*,*N*′-dibutyl-3,4,9,10-perylenetetracarboxylic Diimides (4): A suspension of **2** (850 mg, 1.55 mmol) obtained from the above reaction, *n*-butylamine (0.50 mL, 5.1 mmol), and acetic acid (500 mg, 8.33 mmol) in *N*-methyl-2-pyrrolidinone (NMP; 15 mL) was stirred at 85 °C under N_2 for 12 h. After cooling the mixture to room temperature, it was poured into aqueous HCl (10 vol.-%, 100 mL) and the precipitate was separated by suction filtration, washed with deionized water until pH 7, washed with MeOH (100 mL), and dried under vacuum. The crude product was purified by silica gel column chromatography (200–300 mesh, 40 cm long and 4 cm diameter) with CH_2Cl_2/petroleum ether (3:1, v/v, R_f = 0.37) as eluent. The orange band was collected and **4** was obtained after evaporation of the solvent as a brown powder (0.64 g, 56%). The regioisomeric 1,7- and 1,6-dibromoperylene bisimides could not be separated by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (m, 2 H), 8.94 (d, 2 H), 8.72 (m, 2 H), 4.26–4.19 (m, 4 H), 1.79–1.70 (m, 4 H), 1.50–1.43 (m, 4 H), 1.00 (t, 6 H) ppm. HRMS: calcd. for $C_{32}H_{25}Br_2N_2O_4$ [M + H]$^+$ 661.0082; found 661.0153.

Dibromo-*N*,*N*′-dicyclohexyl-3,4,9,10-perylenetetracarboxylic Diimides (5): Compound **2** (850 mg, 1.55 mmol), cyclohexylamine (0.58 mL, 5.0 mmol), and acetic acid (500 mg, 8.33 mmol) in *N*-methyl-2-pyrrolidinone (NMP; 20 mL) were stirred at 85 °C under N_2 for 12 h. After cooling the mixture to room temperature and pouring into aqueous HCl (10 vol.-%, 100 mL), the precipitate was separated by suction filtration, washed with deionized water until pH 7, washed with MeOH (100 mL), and dried under vacuum. The crude product was purified by silica gel column chromatography (200–300 mesh, 40 cm long and 4 cm diameter) with $CHCl_3$/*n*-hexane (4:1, v/v, R_f = 0.61) as eluent and **5** was obtained after evaporation of the solvent as a red powder (0.72 g, 65%). The regioisomeric 1,7- and 1,6-dibromoperylene bisimides could not be separated by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (m, 2 H), 8.88 (s, 2 H), 8.67 (m, 2 H), 4.99–5.02 (m, 2 H), 2.51–2.59 (m, 4 H), 1.96–1.87 (m, 4 H), 1.77–1.74 (m, 6 H), 1.36–1.52 (m, 6 H) ppm. HRMS: calcd. for $C_{36}H_{29}Br_2N_2O_4$ [M + H]$^+$ 713.0395; found 713.9841.

1,7-Dibromo-*N*,*N*′-Bis[2-(diethylamino)ethyl]-3,4,9,10-perylenetetracarboxylic Diimide (6a): Compound **2** (950 mg, 1.73 mmol), 2-(diethylamino)ethylamine (0.70 mL, 5.0 mmol), and acetic acid (500 mg, 8.33 mmol) in H_2O/2-propanol (1:1, v/v, 20 mL) were stirred at 80 °C under N_2 for 24 h. The mixture was cooled to room temperature. After evaporation of the solvent, CH_2Cl_2 (80 mL) was added. Insoluble solid was removed by filtration and then the filtrate was concentrated to 20–30 mL. The crude product was purified by silica gel column chromatography (200–300 mesh, 30 cm long and 4 cm diameter) with CH_2Cl_2/MeOH (10:1, v/v, R_f = 0.40) as eluent and **6a** was obtained after evaporation of the solvent as a red powder (0.79 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (d, 2 H), 8.82 (s, 2 H), 8.60 (d, 2 H), 4.31 (t, 4 H), 2.87 (s, 4 H), 2.73 (s, 8 H), 1.09 (s, 12 H) ppm. HRMS: calcd. for $C_{36}H_{35}Br_2N_2O_4$ [M + H]$^+$ 747.0926; found 747.0991.

1,7-Dibromo-*N*,*N*′-Bis[2-(dimethylamino)ethyl]-3,4,9,10-perylenetetracarboxylic Diimides (7a): Compound **2** (950 mg, 1.73 mmol), 2-(dimethylamino)ethylamine (0.50 mL, 5.3 mmol), and acetic acid (500 mg, 8.33 mmol) in H_2O/2-propanol (2:1, v/v, 20 mL) were stirred at 80 °C under N_2 for 18 h. After cooling the mixture to room temperature and evaporation of the solvent, CH_2Cl_2 (60 mL) was added. The brownish red solution was washed with a saturated aqueous NaCl solution (30 mL × 3) and water (30 mL × 3) and then dried with anhydrous sodium sulfate. The crude product was purified by silica gel column chromatography (200–300 mesh, 30 cm long and 4 cm diameter) with CH_2Cl_2/MeOH (10:1, v/v, R_f = 0.37) as eluent and **7a** was obtained after evaporation of the solvent as a red powder (0.72 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.37 (d, 2 H), 8.82 (s, 2 H), 8.60 (d, 2 H), 4.32 (t, 4 H), 2.70 (t, 4 H), 2.35 (s, 12 H) ppm. HRMS: calcd. for $C_{32}H_{27}Br_2N_2O_4$ $[M + H]^+$ 691.0300; found 961.0356.

1,7-Dibromoperylene-3,4,9,10-tetracarboxylic Dianhydride (2a): KOH (4.0 g, 70 mmol) was dissolved in 2-propanol (80 mL) at 60 °C. After cooling the solution to room temperature, **7a** (0.60 g, 0.87 mmol) was added under N_2 and then the mixture was stirred at 80 °C for 12 h. The obtained solution changed from brownish red to green after cooling to room temperature. Acetic acid (100 mL) was poured slowly into the above solution and stirred at room temperature for 8 h. The red precipitate was separated by centrifugation (4000 rpm, 3 min), washed with *n*-hexane, and then dried under vacuum. The red solid was finally dissolved in concentrated sulfuric acid (20 mL) and then dipped carefully into H_2O (100 mL) at 0 °C. After separation by centrifugation (4000 rpm, 3 min), the solid was washed with H_2O and then dried under vacuum to give **2a** (0.45 g, 94%), which could not be purified owing to its insolubility in organic solvents.

1,7-Dibromo-*N*,*N*′-dibutyl-3,4,9,10-perylenetetracarboxylic Diimides (4a): A suspension of **2a** (0.17 g, 0.31 mmol) obtained from the above reaction, *n*-butylamine (0.10 mL, 1.0 mmol), and acetic acid (100 mg, 1.67 mmol) in *N*-methyl-2-pyrrolidinone (NMP; 5 mL) was stirred at 85 °C under N_2 for 12 h. After purification following the same method as that used for the synthesis of **4**, **4a** was obtained as a brown powder (0.18 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (d, 2 H), 8.86 (s, 2 H), 8.64 (d, 2 H), 4.18–4.12 (t, 4 H), 1.72–1.64 (m, 4 H), 1.40 (m, 4 H), 0.93 (t, 6 H) ppm.

1,7-Bis(*n*-butylthio)-*N*,*N*′-dibutyl-3,4,9,10-perylenetetracarboxylic Diimides (8): A mixture of **4a** (132 g, 0.2 mmol), *o*-xylene (5 mL), anhydrous potassium carbonate (304 mg, 2.2 mmol), CTAB (7 mg, 0.02 mmol), and *n*-butanethiol (0.17 mL, 1.6 mmol) was heated to 80 °C under N_2. The reaction mixture was kept at this temperature for about 12 h and then the solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh, 30 cm long and 4 cm diameter) with CH_2Cl_2/*n*-hexane (10:1, v/v, R_f = 0.37) as eluent. The red fraction was collected and after evaporation of the solvent, **8** was collected as an dark purple powder (52.5 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, 2 H), 8.79 (s, 2 H), 8.69 (d, 2 H), 4.27–4.22 (t, 4 H), 3.22 (m, 4 H), 1.77 (m, 4 H), 1.71–1.64 (m, 4 H), 1.48 (m, 8 H), 1.01 (t, 6 H), 0.91 (t, 6 H) ppm. HRMS: calcd. for $C_{40}H_{43}N_2O_4S_2$ $[M + H]^+$ 679.2586; found 679.2659.

1,7-Dipiperidinyl-*N*,*N*′-dibutyl-3,4,9,10-perylenetetracarboxylic Diimides (9): A mixture of **4a** (99 mg, 0.15 mmol) and piperidine (5.9 mL, 60 mmol) was heated to 55 °C under N_2. The reaction mixture was kept at this temperature for about 24 h and then the solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (200–300 mesh, 30 cm long and 4 cm diameter) with $CHCl_3$/petroleum ether (40:1, v/v, R_f = 0.48) as eluent. The green fraction was collected and after evaporation of the solvent, **9** was collected as a green powder (67.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (d, 2 H), 8.45–8.41 (m, 4 H), 4.24–4.19 (t, 4 H), 3.49 (m, 4 H), 2.97–2.86 (m, 4 H), 1.81–1.70 (m, 16 H), 1.48 (m, 4 H), 1.00 (t, 6 H) ppm. Good agreement was found with the literature.[17]

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[1] a) A. Lv, S. R. Puniredd, J. Zhang, Z. Li, H. Zhu, W. Jiang, H. Dong, Y. He, L. Jiang, Y. Li, *Adv. Mater.* **2012**, *24*, 2626–2630; b) C. Backes, C. D. Schmidt, K. Rosenlehner, F. Hauke, J. N. Coleman, A. Hirsch, *Adv. Mater.* **2010**, *22*, 788–802; c) T. Takada, A. Ashida, M. Nakamura, M. Fujitsuka, T. Majima, K. Yamana, *J. Am. Chem. Soc.* **2014**, *136*, 6814–6817; d) X. Zhang, S. Rehm, M. M. Safont-Sempere, F. Würthner, *Nat. Chem.* **2009**, *1*, 623–629.

[2] a) T. Heek, F. Würthner, R. Haag, *Chem. Eur. J.* **2013**, *19*, 10911–10921; b) R. Marty, R. Nigon, D. Leite, H. Frauenrath, *J. Am. Chem. Soc.* **2014**, *136*, 3919–3927.

[3] a) K.-R. Wang, D.-S. Guo, B.-P. Jiang, Y. Liu, *Chem. Commun.* **2012**, *48*, 3644–3646; b) J. t. Schiphorst, A. M. Kendhale, M. G. Debije, C. Menelaou, L. M. Herz, A. P. Schenning, *Chem. Mater.* **2014**, *26*, 3876–3878; c) D. Chaudhuri, D. Li, Y. Che, E. Shafran, J. M. Gerton, L. Zang, J. M. Lupton, *Nano Lett.* **2011**, *11*, 488–492; d) A. W. Hains, H.-Y. Chen, T. H. Reilly III, B. A. Gregg, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4381–4387; e) J. Zhang, S. Singh, D. K. Hwang, S. Barlow, B. Kippelen, S. R. Marder, *J. Mater. Chem. C* **2013**, *1*, 5093–5100.

[4] D. Ke, A. Tang, C. Zhan, J. Yao, *Chem. Commun.* **2013**, *49*, 4914–4916.

[5] a) D. Ley, C. X. Guzman, K. H. Adolfsson, A. M. Scott, A. B. Braunschweig, *J. Am. Chem. Soc.* **2014**, *136*, 7809–7812; b) F. Schlosser, J. Sung, P. Kim, D. Kim, F. Würthner, *Chem. Sci.* **2012**, *3*, 2778–2785.

[6] a) R. K. Dubey, A. Efimov, H. Lemmetyinen, *Chem. Mater.* **2011**, *23*, 778–788; b) R. K. Dubey, M. Niemi, K. Kaunisto, A. Efimov, N. V. Tkachenko, H. Lemmetyinen, *Chem. Eur. J.* **2013**, *19*, 6791–6806.

[7] a) X. Zhang, S. Pang, Z. Zhang, X. Ding, S. Zhang, S. He, C. Zhan, *Tetrahedron Lett.* **2012**, *53*, 1094–1097; b) P. Rajasingh, R. Cohen, E. Shirman, L. J. Shimon, B. Rybtchinski, *J. Org. Chem.* **2007**, *72*, 5973–5979.

[8] a) M. J. Ahrens, M. J. Tauber, M. R. Wasielewski, *J. Org. Chem.* **2006**, *71*, 2107–2114; b) G. Goretzki, E. S. Davies, S. P. Argent, W. Z. Alsindi, A. J. Blake, J. E. Warren, J. McMaster, N. R. Champness, *J. Org. Chem.* **2008**, *73*, 8808–8814.

[9] F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher, D. Stalke, *J. Org. Chem.* **2004**, *69*, 7933–7939.

[10] S. Sengupta, R. K. Dubey, R. W. Hoek, S. P. van Eeden, D. D. Gunbas, F. C. Grozema, E. J. Sudhölter, W. F. Jager, *J. Org. Chem.* **2014**, *79*, 6655–6662.

[11] M. Queste, C. Cadiou, B. Pagoaga, L. Giraudet, N. Hoffmann, *New J. Chem.* **2010**, *34*, 2537–2545.

[12] M. Franceschin, N. Borbone, G. Oliviero, V. Casagrande, M. Scuotto, T. Coppola, S. Borioni, L. Mayol, G. Ortaggi, A. Bianco, *Bioconjugate Chem.* **2011**, *22*, 1309–1319.

[13] S. Dey, A. Efimov, H. Lemmetyinen, *Eur. J. Org. Chem.* **2012**, 2367–2374.

[14] Y. Li, Z. Qing, Y. Yu, T. Liu, R. Jiang, Y. Li, *Chem. Asian J.* **2012**, *7*, 1934.

[15] a) B. Dhokale, P. Gautam, R. Misra, *Tetrahedron Lett.* **2012**, *53*, 2352–2354; b) Á. J. Jiménez, F. Spänig, M. S. Rodríguez-Morgade, K. Ohkubo, S. Fukuzumi, D. M. Guldi, T. Torres, *Org. Lett.* **2007**, *9*, 2481–2484.
[16] C. Zhao, Y. Zhang, R. Li, X. Li, J. Jiang, *J. Org. Chem.* **2007**, *72*, 2402–2410.
[17] J. Feng, D. Wang, H. Wang, D. Zhang, L. Zhang, X. Li, *J. Phys. Org. Chem.* **2011**, *24*, 621–629.
[18] L. Fan, Y. Xu, H. Tian, *Tetrahedron Lett.* **2005**, *46*, 4443–4447.
[19] a) H.-Z. Chen, M.-M. Shi, T. Aernouts, M. Wang, G. Borghs, P. Heremans, *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 521–527; b) E. Lucenti, C. Botta, E. Cariati, S. Righetto, M. Scarpellini, E. Tordin, R. Ugo, *Dyes Pigm.* **2013**, *96*, 748–755.
[20] a) W. Jiang, L. Ye, X. Li, C. Xiao, F. Tan, W. Zhao, J. Hou, Z. Wang, *Chem. Commun.* **2014**, *50*, 1024–1026; b) B. Pagoaga, L. Giraudet, N. Hoffmann, *Eur. J. Org. Chem.* **2014**, 5178–5195; c) Y. Avlasevich, C. Li, K. Müllen, *J. Mater. Chem.* **2010**, *20*, 3814–3826.
[21] a) C. D. Schmidt, C. Böttcher, A. Hirsch, *Eur. J. Org. Chem.* **2007**, 5497–5505; b) H. Langhals, A. Obermeier, *Eur. J. Org. Chem.* **2008**, 6144–6151.
[22] K. D. Belfield, M. V. Bondar, F. E. Hernandez, O. V. Przhonska, *J. Phys. Chem. C* **2008**, *112*, 5618–5622.

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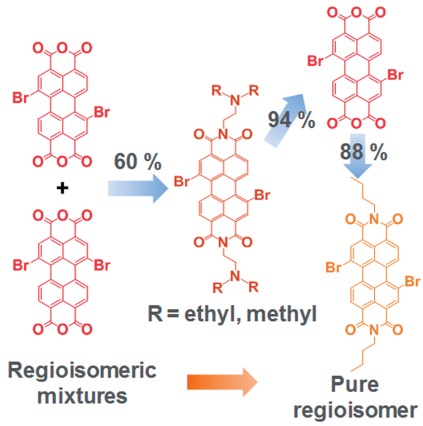
Synthetic Methods

1,7-Dibromo-substituted perylene bisimides have been isolated from regioisomeric mixtures by column chromatography in yields of at least 60%. The 1,7-disubstituted intermediates can provide a convenient and efficient approach to novel perylene bisimide derivatives.



Keywords: Dyes/Pigments / Regioselectivity / Separation methods / UV/Vis spectroscopy

