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Preparation and Characterization of Regioisomerically Pure 1,7-Disubstituted Perylene Bisimide Dyes

Frank Würthner,*,† Vladimir Stepanenko,† Zhijian Chen,† Chantu R. Saha-Möller,†
Nikolaus Kocher,‡ and Dietmar Stalke‡

Institutes of Organic Chemistry and Inorganic Chemistry, University of Würzburg,
Am Hubland, 97074 Würzburg, Germany

wuerthner@chemie.uni-wuerzburg.de

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A detailed study on bromination and subsequent imidization of perylene bisanhydride with cyclohexylamine is reported. The present results reveal that previously reported 1,7-difunctionalized perylene bisimides are presumably contaminated with the respective 1,6 regioisomers. *N*,*N*′-Dicyclohexyl-1,7-dibromoperylene bisimide *1,7*-**3** is obtained for the first time in isomerically pure form, and its structure is unequivocally confirmed by X-ray analysis. By using regioisomerically pure 1,7-dibromoperylene bisimide *1,7*-**3**, 1,7-dipyrrolidinylperylene bisimides **4a**–**c** and 1,7-dipyrrolidinylperylene bisanhydride **5** as well as the unsymmetrically difunctionalized 1-bromo-7-pyrrolidinyl- and 1-cyano-7-pyrrolidinylperylene bisimides **7** and **8** are synthesized in good yield.

Introduction

Derivatives of perylene-3,4:9,10-tetracarboxylic acid bisimide are of increasing interest as functional dyes for applications in molecular electronic devices such as photovoltaic cells,[1] organic field-effect transistors (OFETs),[2] and light-emitting diodes (OLEDs).[3] These dyes were also used in electrophotography (xerographic photoreceptors),[4] fluorescent light collectors,[5] and lasers.[6] Furthermore, liquid crystallinity of perylene bisimides has been recently demonstrated[7] as well as nano- and mesoscopic supramolecular architectures.[8]

Distinct optical and electronic properties are required for the application of perylene bisimides in optoelectronics. The desired properties may be achieved by proper functionalization of perylene bisimide. The chemical modification at imide groups does not significantly effect the optical and electronic properties of this chromophore because of nodes in the HOMO and LUMO orbitals at the imide nitrogen atoms.[9,10] However, these properties are drastically changed on functionalization of the perylene core with electron-donor or -acceptor groups. Such core-functionalized perylene bisimides are usually synthesized from the respective halogenated, in particular, brominated, derivatives in the case of difunctionalized perylene bisimides. In a 1997 patent,[11] BASF disclosed a procedure for the bromination of perylene bisanhydride **1** and subsequent imidization of brominated product as well as exchange of bromine atoms in bisimides by phenoxy and alkyne groups. This patent claimed that the bromination of perylene bisanhydride **1** under the conditions applied forms selectively 1,7-dibromoperylene bisanhydride *1,7*-**2** (Scheme 1), and consequently, the subsequent imidiza-

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* To whom correspondence should be addressed. Tel: + 49 (0)931-8885340. Fax: + 49-(0)931-8884756.

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‡ Institute of Inorganic Chemistry.

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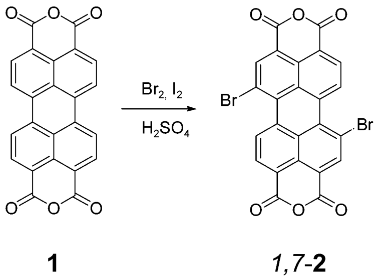
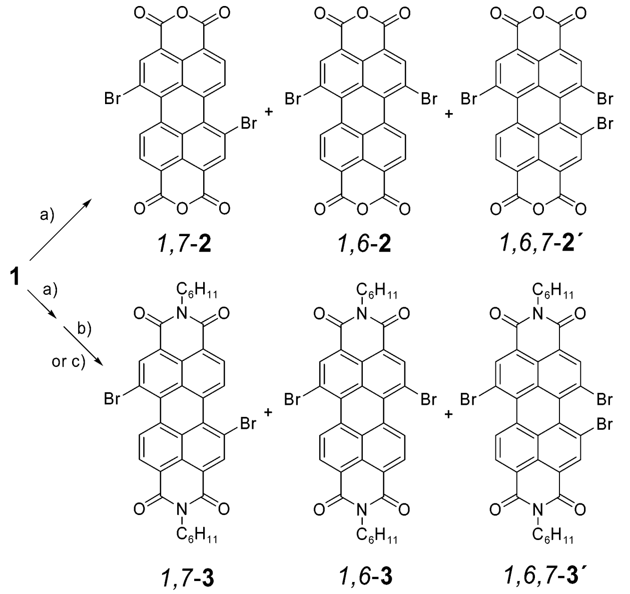
SCHEME 1. Bromination of Perylene Bisanhydride (1) According to the BASF Patent[11]



SCHEME 2. Isomeric Products Formed in the Bromination and Subsequent Imidization of Perylene Bisanhydride 1[a]



[a] Reagents and conditions: (a)[11] Br_2, I_2 (catalytic), 100% H_2SO_4, 85 °C, 11 h; (b)[11] $H_{11}C_6$-NH_2, *N*-methylpyrrolidinone, 85 °C, 6 h; (c) $H_{11}C_6$-NH_2, H_2O/*n*-PrOH (2:1), Ar, 80 °C, 10 h.

tion leads to isomerically pure 1,7-dibrominated bisimides. In the past years, numerous disubstituted perylene bisimides (PBIs) with interesting functionalities,[12] including liquid crystalline[13,14] PBIs, dendrimers,[15] organogels,[16] and polymers,[17] were synthesized from 1,7-dibrominated perylene bisimides prepared according to the patent procedure[11] and applied in light-harvesting systems,[16] LEDs,[17] molecular switches,[18] wires,[19] and logic gates.[20]

Our results presented here reveal that the previously reported difunctionalized perylene bisimides are apparently mixtures of 1,7 and 1,6 regioisomers rather than isomerically pure compounds. Surprisingly, only one[13b] of the above-cited publications has drawn attention to this problem, while the other reports only mentioned 1,7-disubstituted perylene bisimides. The reason for this may be that, on one hand, the precursor of difunctionalized perylene bisimides, i.e., 1,7-dibromoperylene bisanhydride *1,7*-**2**, is virtually insoluble in any organic solvent and, thus, its characterization was made only by elemental analysis and mass spectrometry which do not differentiate regioisomers, and on the other hand, isomeric mixtures of the subsequently prepared perylene bisimides can be observed only by high-field (> 400 MHz) ^{1}H NMR. Thus, in one of our earlier publications[14] on liquid-crystalline PBIs we did not recognize the presence of isomeric impurities on the basis of 400 MHz ^{1}H NMR. In the course of our intensive research work on perylene bisimide chemistry, we became meanwhile aware of this problem and have reinvestigated in detail all the steps in the synthesis of disubstituted perylene bisimides to assign unequivocally the respective isomers and to develop methods for their purification. Here, we report that 1,7-dibromoperylene bisimide can be obtained in isomerically pure form, and the nucleophilic replacement of bromine atoms affords pure difunctionalized bisimide derivatives.

Results and Discussion

The bromination of perylene bisanhydride **1** was repeated according to the patent procedure[11] [Scheme 2, reaction conditions (a)], and the crude product, which is insoluble in organic solvents, was investigated by 600 MHz ^{1}H NMR spectroscopy in concentrated D_2SO_4 (96−98% in D_2O). Three sets of signals with different intensities were observed in the ^{1}H NMR spectrum (Figure 1) indicating that at least three different products are formed in the bromination of bisanhydride **1**. In the region between 8.7 and 9.1 ppm three doublets and three singlets appear, and further, three doublets are overlapped to a multiplet at 9.65−9.75 ppm. This signal pattern implies that 1,7- and 1,6-dibromoperylene bisanhydrides (*1,7*-**2** and *1,6*-**2**) and tribrominated perylene *1,6,7*-**2′** (Scheme 2) are formed in the bromination of perylene bisanhydride **1**. (Further evidence for structural assignment of these compounds is provided below.) The integration areas of the doublets at 8.79, 8.82, and 8.89 ppm (Figure 1) reveal that *1,7*-**2**, *1,6*-**2**, and *1,6,7*-**2′** are fomed in a ratio of ca. 76:20:4.

Since the brominated perylene bisanhydrides are insoluble in organic solvents and, therefore, could not be purified by any means, the crude product mixture was used for the subsequent imidization with cyclohexylamine under the reaction conditions reported in the

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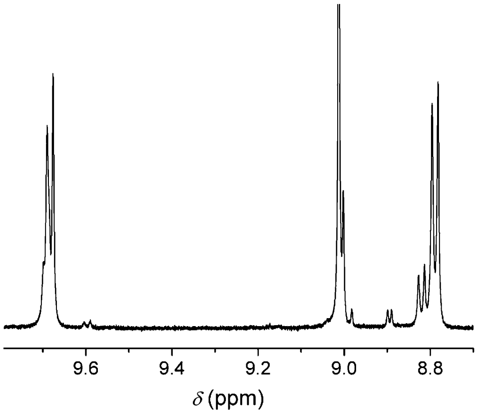

FIGURE 1. ^{1}H NMR (600 MHz, D_2SO_4, calibrated for TMS) spectrum of bromination products of perylene bisanhydride **1**.

BASF patent [Scheme 2, reaction conditions (b)].[11] As expected, the imidization afforded a mixture of 1,7- and 1,6-dibromoperylene bisimides (*1,7*-**3** and *1,6*-**3**) and tribrominated bisimide *1,6,7*-**3′**. For the imidization of perylene bisanhydride derivatives reaction conditions different from those used in the above-mentioned patent were employed;[15b] therefore, we have also carried out the imidization of brominated products of perylene bisanhydride **1** in a 2:1 mixture of H_2O/*n*-PrOH, instead of *N*-methylpyrrolidinone, at 80 °C [Scheme 2, reaction conditions (c)], and similar results were obtained as under the reaction conditions (b). In contrast to brominated perylene bisanhydrides **2**, the respective perylene bisimides **3** are soluble in organic solvents to facilitate their further purification. The silica gel column chromatography of the product mixture obtained after imidization of **2** with CH_2Cl_2 as eluent allowed the separation of the minor component tribrominated bisimide *1,6,7*-**3′**, which was obtained in ca. 1% yield and characterized by ^{1}H and ^{13}C NMR and MS. However, the regioisomeric 1,7- and 1,6-dibromoperylene bisimides (*1,7*-**3** and *1,6*-**3**) could not be separated by column chromatography, and a 80:20 mixture (determined by 600 MHz ^{1}H NMR) of *1,7*-**3** and *1,6*-**3** was obtained in 61% yield. Fortunately, the major regioisomer *1,7*-**3** could be separated by repetitive recrystallization of the 80:20 mixture of *1,7*-**3** and *1,6*-**3** from CH_2Cl_2/MeOH (1:1). The recrystallization process was monitored by 600 MHz ^{1}H NMR spectroscopy (Figure 2) to assess the number of recrystallization steps required for complete purification. After three successive recrystallizations, the regioisomer *1,7*-**3** could be obtained in pure form as the ^{1}H NMR spectrum (Figure 2c) reveals. In mother liquor, the minor isomer *1,6*-**3** is enriched as the NMR spectrum shows (Figure 2d); however, the latter could not be obtained in pure form. It is noteworthy that the characteristic signals, in particular the doublets, of the regioisomers *1,7*-**3** and *1,6*-**3** are only separated in high-field ^{1}H NMR spectra since the chemical shifts differ very little (0.006 ppm for the doublets at 9.42−9.46 ppm; see Figure 2a), while at lower field these signals overlap. This might be the reason why in former publications on 1,7-difunctionalized perylene bisimides the problem of regioisomers was not recognized. Although our NMR data are in agreement with those reported[13b,15b] for 1,7-dibromoperylene bisimides, an unequivocal assignment of the NMR signals to the individual regioisomers *1,7*-**3** and *1,6*-**3** is not possible due to the symmetry of both isomers. Fortunately, single crystals of the major isomer, obtained after repetitive recrystallization (Figure 2c), were grown on covering its CH_2Cl_2 solution by MeOH layer. The X-ray analysis confirmed unequivocally the structure of the major isomer as 1,7-dibromoperylene bisimide *1,7*-**3** (Figure 3; note that the numbering of the carbon atoms in the anisotropic displacement parameter plot is not in accordance with the nomenclature of the compound). The fact that the imidization of the crude bromination products of perylene bisanhydride **1** with cyclohexylamine (Scheme 2) afforded *N,N′*-dicyclohexyl-1,7-dibromoperylene bisimide *1,7*-**3** as the major product, it can be concluded that the corresponding 1,7-dibromoperylene bisanhydride *1,7*-**2** is the major product in the bromination of perylene bisanhydride **1**. Thus, the structures of the major products of bromination of **1** and subsequent imidization are now unequivocally assigned.

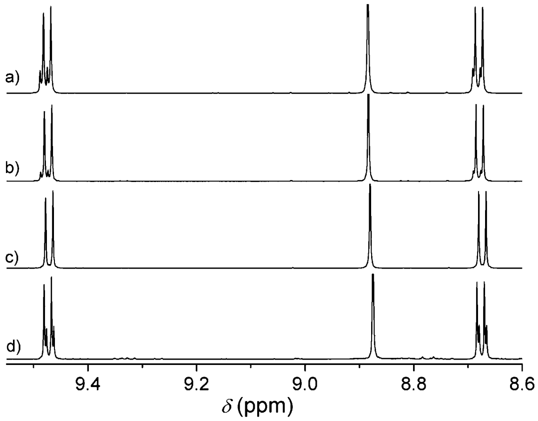

FIGURE 2. ^{1}H NMR spectroscopic monitoring of recrystallization; 600 MHz ^{1}H NMR spectra: (a) regioisomeric mixture of *1,7*-**3** and *1,6*-**3** before recrystallization, (b) after one and (c) after three repetitive recrystallizations, (d) spectrum of mother liquor of first recrystallization of the residue obtained after condensation of the solution of first recrystallization.

To our knowledge, this is the first crystal structure reported for 1,7-disubstituted perylene bisimide dyes. The selected crystallographic data of *1,7*-**3** are given in ref 21, and the characteristic features of the crystal are described below.

Dibromoperylene bisimide *1,7*-**3** crystallizes in the triclinic space group *P*-1. The central six-membered ring of *1,7*-**3** is twisted (Figure 3, right part) with a dihedral angle of 24° associated with bay area carbon atoms C8−C9−C10−C11 and C18−C19−C20−C1, which is almost identical with the dihedral angle of previously reported tetraphenoxy-substituted diazadibenzoperylenes[22] and 14° smaller than that observed for tetrachloro-substituted perylene bisimides.[23] This twist also induces axial chirality in this 1,7-disubstituted perylene bisimide dye. However, *1,7*-**3** crystallizes as a racemate in a centrosymmet-

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(21) Selected crystallographic data for 1,7-dibromoperylene bisimide *1,7*-**3**. Crystal system: triclinic, space group: *P*-1, unit cell dimensions: a = 10.9311(8) Å, b = 14.0064(10) Å, c = 21.9075(16) Å, α = 72.6050(10)°, β = 81.3230(10)°, γ = 70.8890(10)°, V 3019.1(4) Å^3, Z = 2, density (calcd) 1.656 g/cm^3, R indices [$I > 2\sigma(I)$]: R1 = 0.0558, wR2 = 0.1515, R indices (all data): R1 = 0.0775, wR2 = 0.1665.

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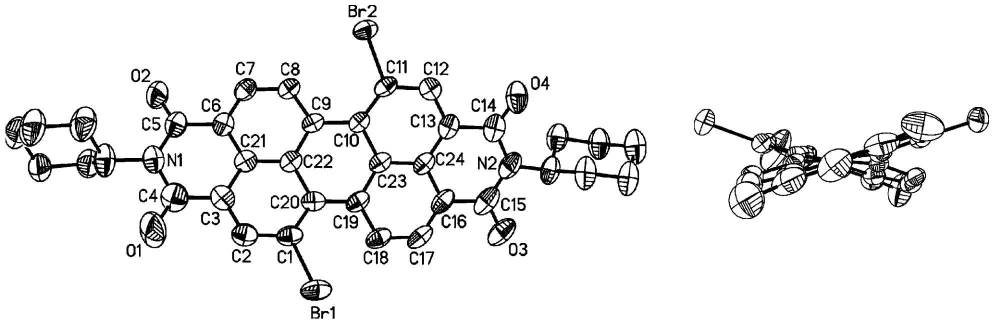


FIGURE 3. Molecular structure of 1,7-dibromoperylene bisimide *1,7*-**3** (left) and view along the N−N axis showing the twisted perylene backbone (right). The anisotropic displacement parameters are depicted at the 50% probability level.

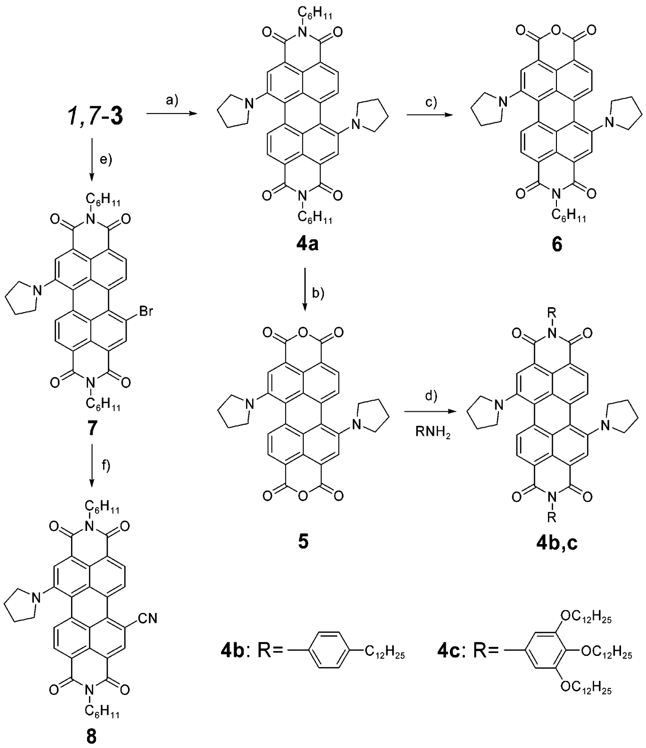
ric space group. All C−C bond lengths of the perylene backbone range between 1.35 and 1.46 Å, indicating the presence of π-conjugation for all C−C bonds. The longest bonds in the perylene unit are the C9−C10 and C19−C20 bonds, which connect the two naphthalene units at a length of 1.46 Å. This bond length is identical with that observed for the parent perylene bisimide (without substituents in the bay area),[24] indicating that, although the perylene unit in *1,7*-**3** is significantly twisted, the degree of conjugation is similar in both disubstituted and unsubstituted perylene bisimides.

Once we have obtained reasonable amounts of isomerically pure 1,7-dibromoperylene bisimide *1,7*-**3**, this substrate was used for the synthesis of 1,7-difunctionalized perylene bisimides and bisanhydrides. The transformations are shown in Scheme 3.

The nucleophilic substitution of regioisomerically pure 1,7-dibromoperylene bisimide *1,7*-**3** with pyrrolidine at 55 °C according to Wasielewski's method[12a] (Scheme 3 (a)) afforded the corresponding dipyrrolidinyl bisimide **4a** as a green solid in 67% yield after column chromatography. Once the substitution reaction was carried out at 46 °C, the monopyrrolidinyl bisimide **7** was obtained in 28% yield after column chromatographic purification. The latter substrate was converted to the hitherto unknown unsymmetrically difunctionalized monocyano monopyrrolidinyl bisimide **8** by cyanation with $Zn(CN)_2$ in the presence of Pd(0) catalyst according to standard literature procedure (Scheme 3 (f)).[12e]

The saponification of **4a** in 2-propanol with 100-fold excess of KOH afforded the hitherto unknown 1,7-dipyrrolidinylperylene bisanhydride **5** in 62% yield. This novel building block was successfully applied for the synthesis of regioisomerically pure 1,7-dipyrrolidinylperylene bisimides. Thus, the condensation reaction of **5** with 3,4,5-tridodecyloxyaniline and 4-dodecylaniline according to standard procedure[25] gave the corresponding difunctionalized symmetrical perylene bisimides **4b** and **4c** in 44% and 33% yield, respectively.

SCHEME 3. Chemical Transformations of Isomerically Pure 1,7-Dibromoperylene Bisimide *1,7*-3[a]



[a] Reagents and conditions: (a) pyrrolidine, 55 °C, Ar, 24 h, 67% of **4a**; (b) KOH (100 equiv), -*i*PrOH, reflux, 2 h, 62% of **5**; (c) KOH (50 equiv), *i*-PrOH/H_2O (6:1), reflux, 2.75 h, 88% of **6**; (d) 4-dodecylaniline or 3,4,5-tridodecyloxyaniline, $Zn(OAc)_2$, quinoline, 180 °C, 18−24 h, 44% of **4b** and 33% for **4c**; (e) pyrrolidine, 46 °C, Ar, 24 h, 28% of **7**; (f) $Pd_2(dba)_3$, 1,1-bis(diphenylphosphino)ferrocene, $Zn(CN)_2$, dioxane, 110 °C, Ar, 20 h, 84% of **8**.

Since perylene monoimide monoanhydrides are important starting materials for the synthesis of unsymmetrical perylene bisimide,[26] we have searched for reaction conditions for partial saponification of **4a** to obtain pure dipyrrolidinyl-functionalized perylene monoimide monoanhydride **6** that may serve as a building block for the synthesis of electron-donor functionalized unsymmetrical perylene bisimides. After optimization of reported reaction conditions,[12b] a partial saponification of **4a** was achieved in a 6:1 mixture of 2-propanol−water with 50-fold excess of KOH under reflux. Under these reaction conditions, bisimide **4a** was converted up to 45% after ca. 2.75 h and only monoimide monoanhydride **6** was formed. The prolongation of reaction time leads to the generation of bisanhydride **5**. Therefore, the reaction was terminated after this time, and column chromatographic purification of the crude mixture afforded **6** in

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analytically pure form in 88% yield (relative to the converted amount of **4a**), and the unreacted starting material **4a** was recovered.

Conclusions

Our detailed study has shown that the bromination and subsequent imidization of perylene bisanhydride **1** with cyclohexylamine leads to a mixture of regioisomeric 1,7- and 1,6-dibromoperylene bisimides *1,7*-**3** and *1,6*-**3** and tribrominated bisimide *1,6,7*-**3′**. Since the regioisomers *1,7*-**3** and *1,6*-**3** are only detectable by high-field ^{1}H NMR spectroscopy and cannot be separated by conventional silica gel column chromatography, we suspect that the previously reported 1,7-difunctionalized perylene bisimides, which were synthesized from 1,7-dibromoperylene bisimide obtained according to the BASF patent,[11] are contaminated with the respective 1,6 isomers. Thus, one of the objectives of this contribution is to draw attention of chemists as well as material scientists to this apparently less considered problem of regioisomeric impurity in 1,7-difunctionalized perylene bisimide probes.

We have obtained isomerically pure 1,7-dibromoperylene bisimide *1,7*-**3** after column chromatographic removal of tribrominated bisimide *1,6,7*-**3′** and three successive recrystallization of a ca. 80:20 mixture of *1,7*-**3** and *1,6*-**3**. The structure of *1,7*-**3** was confirmed by X-ray analysis. Although the present purification method is rather cumbersome, to date no attractive alternative is available for the preparation of regioisomerically pure 1,7-dibromoperylene bisimides that are important precursors for the synthesis of 1,7-difunctionalized perylene bisimides. Regioisomerically pure 1,7-dibromoperylene bisimide *1,7*-**3** has shown to be a versatile building block for the synthesis of pure 1,7-difunctionalized perylene bisimide derivatives. In this work, we have shown that the two bromine substituents can be exchanged even in a sequential manner leading to donor−acceptor substituted PBIs. Partial saponification to imide anhydrides is possible as well. Therefore, we anticipate that on the basis of this study several pure PBI derivatives with interesting properties will become available.

Experimental Section

General Methods. Solvents and reagents were obtained from commercial sources and used as received. NMR spectra were recorded at room temperature on 600 MHz (^{1}H) and 400 MHz spectrometers. The solvents for spectroscopic studies were of spectroscopic grade and used as received. UV/vis spectra were measured on a spectrophotometer equipped with a temperature controller. The steady-state fluorescence spectra were measured on a convertional spectrofluorometer and fluorescence quantum yields were determined by the optically dilute method with fluorescein (Φ_f = 0.92 in 1 N NaOH aqueous solution) and cresyl violet (Φ_f = 0.54 in methanol) as reference.

Bromination of Perylene Bisanhydride 1.[11] A mixture of 31.3 g (80.0 mmol) of perylene-3,4:9,10-tetracarboxylic acid bisanhydride (**1**) and 472 g of 100 wt % sulfuric acid was stirred for 12 h at room temperature, and subsequently I_2 (0.77 g, 3.0 mmol) was added. The reaction mixture was heated to 85 °C, and 28.2 g (176 mmol) of bromine was added dropwise over a time period of 8 h. After bromine addition, the reaction mixture was heated for an additional 10 h at 85 °C and cooled to room temperature. The excess bromine was removed by a gentle stream of N_2 gas, and 65 mL of water was added carefully. The resulting precipitate was separated by filtration through a G4 funnel, washed with 300 g of 86% sulfuric acid and a large amount of water, and dried in a vacuum to give 42.0 g (95%) of a red powder. The crude product could not be purified since it is insoluble in organic solvents. The analysis of this crude product by 600 MHz ^{1}H NMR in concentrated D_2SO_4 (96−98% in D_2O) revealed that 1,7- and 1,6-dibromo- and 1,7,6-tribromoperylene bisanhydrides were formed in a ratio of 76:20:4 (Figure 1). MS (EI, 70 eV) *m/z*: 547.8 (45.9), 548.8 (16.0), 549.8 (92.0), 550.1 (24.2), 551.8 (45.9) [M$^+$] (calcd 550.1). HRMS (EI): calcd for $C_{24}H_6Br_2O_6$ 547.8525, found 547.8523.

1,7-Dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisanhydride (*1,7*-2). ^{1}H NMR (600 MHz, D_2SO_4, calibrated for TMS): δ = 9.68 (d, 2H, J = 8.2 Hz), 9.01 (s, 2H), 8.79 (d, 2H, J = 8.3 Hz).

1,6-Dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisanhydride (*1,6*-2). ^{1}H NMR (600 MHz, D_2SO_4, calibrated for TMS): δ = 9.70 (d, 2H, J = 8.1 Hz), 8.98 (s, 2H), 8.82 (d, 2H, J = 8.1 Hz).

Imidization of Crude Bromination Product.[11] A suspension of brominated perylene bisanhydrides (0.95 g, 1.72 mmol) obtained in the above reaction, cyclohexylamine (0.502 g, 5.07 mmol), and acetic acid (0.50 g, 8.33 mmol) in 20 mL of *N*-methyl-2-pyrrolidinone was stirred at 85 °C under Ar for 6 h. After the mixture was cooled to room temperature, the precipitate was separated by filtration, washed with 100 mL of MeOH, and dried in a vacuum. The crude product was purified by silica gel column chromatography with CH_2Cl_2 as eluent. The first band was collected and after evaporation of solvent, and *N,N′*-dicyclohexyl-1,6,7-tribromoperylene bisimide *1,6,7*-**3′** was obtained as a red powder (13 mg, 1%). The second band contained a mixture of *N,N′*-dicyclohexyl-1,7- and -1,6-dibromoperylene bisimide (*1,7*-**3** and *1,6*-**3**) as a red powder (755 mg, 61%), and 600 MHz ^{1}H NMR analysis revealed a 80:20 ratio. The regioisomeric dibromoperylene bisimides *1,7*-**3** and *1,6*-**3** could not be separated by column chromatography.

Regioisomerically pure 1,7-dibromoperylene bisimide was obtained by repetitive crystallization. In a typical procedure, 450 mg of the 80:20 mixture of *N,N′*-dicyclohexyl-1,7- and 1,6-dibromoperylene bisimide was dissolved in 100 mL of CH_2Cl_2. The solution was poured into a cylinder-shaped glass container (diameter: 5 cm, height: 14 cm) through a glass funnel with a filter paper, and 120 mL MeOH was very carefully layered on the top of CH_2Cl_2 solution by a syringe. The container was sealed and kept at room temperature for 2 weeks to grow red crystals (280 mg, 62%). The recrystallization was repeated two more times to obtained pure 1,7-dibromoperylene bisimide *1,7*-**3** (100 mg, 22%).

***N,N′*-Dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide (*1,7*-3).** Mp > 400 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 9.45 (d, 2H, J = 8.2 Hz), 8.86 (s, 2H), 8.65 (d, 2H, J = 8.0 Hz), 5.02 (m, 2H), 2.54 (m, 4H), 1.20−2.00 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.3, 162.7, 137.9, 132.7, 132.6, 129.9, 129.2, 128.4, 127.0, 123.7, 123.3, 120.7, 54.3, 29.1, 26.5, 25.4. MS (EI, 70 eV) *m/z*: 710.0 (20.6), 712.0 (44), 714.0 (22.9) [M$^+$] (calcd 710.0). UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 527 (49 800), 492 (33 700), 466 (13 600), 390 (5300), 276 (26 400). Fluorescence (CH_2Cl_2): λ_{max} = 543 nm, fluorescence quantum yield Φ_f = 0.94. Anal. Calcd for $C_{36}H_{28}Br_2N_2O_4$: C, 60.69; H, 3.96; N, 3.93. Found: C, 60.10; H, 4.00; N, 3.92.

***N,N′*-Dicyclohexyl-1,6,7-tribromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide (*1,6,7*-3′).** Mp > 400 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.41 (d, 1H, J = 8.0 Hz), 8.87 (s, 1H), 8.78 (s, 2H), 8.67 (d, 1H, J = 8.2 Hz), 5.02 (m, 2H), 2.52 (m, 4H), 1.9−1.2 (m, 16H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 163.0, 162.9, 162.6, 162.5, 137.4, 136.6, 136.4, 133.3, 133.1, 131.4, 131.2, 130.8, 130.7, 129.5, 127.9, 125.9, 125.2, 124.2, 123.8, 123.7, 123.4, 123.3, 122.9, 121.3, 54.4, 54.3, 29.2, 29.1, 29.1, 29.0, 26.5, 26.5, 25.4, 25.3. MS (EI, 70 eV) *m/z*: 790.0 (30.5), 791.0 (12.9), 792.0 (30.6), 793.0 (13) [M$^+$]

(calcd 791.3). UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 529 (36 900), 495 (26 000), 424 (8100), 271 (23 000).

***N,N′*-Dicyclohexyl-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisimide (4a).** A mixture of 95.0 mg (0.133 mmol) of *1,7*-**3** and 4.30 g (59.7 mmol) of pyrrolidine was stirred under Ar for 24 h at 55 °C (external). Subsequently, the reaction mixture was poured into 15 mL of 10% HCl under stirring and extracted with methylene chloride (3 × 20 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting precipitate was purified by column chromatography on silica gel (CH_2Cl_2/hexane (40/1, v/v)) to yield 62 mg (67%) of a green solid. Mp > 400 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.41 (s, 2H), 8.31 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 5.04−5.10 (m, 2H), 3.65−3.82 (m, 4H), 2.72−2.89 (m, 4H), 2.56−2.66 (m, 4H), 1.80−2.10 (m, 12H), 1.76−1.78 (m, 6H), 1.20−1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 163.4, 145.4, 132.8, 128.7, 125.5, 122.6, 121.1, 119.7, 118.4, 116.9, 52.7, 51.0, 28.1, 25.6, 24.7, 24.5. MS (EI, 70 eV) *m/z*: 692.3 (100) [M$^+$], 693.3 (48.8) [M$^+$ + H] (calcd 692.3). HRMS (EI): calcd for $C_{44}H_{44}N_4O_4$ 692.3362, found 692.3370. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 700 (38 700), 436 (15 400), 346 (50 600), 314 (24 700), 275 (25 300). Fluorescence (CH_2Cl_2): λ_{max} = 736 nm, fluorescence quantum yield Φ_f = 0.25.

1,7-Dipyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisanhydride (5). A mixture of 100 mg (0.15 mmol) of **4a**, 600 mg (15.0 mmol) of KOH, and 5 mL of *i*-PrOH was brought to reflux. The mixture was stirred for 2 h and poured under stirring into 17 mL of AcOH. The resulting green precipitate was concentrated by centrifugation, washed with water and methanol, and purified by recrystallization from tetrachloroethane/ethyl acetate to give 47 mg (62%) of **5**. Mp > 400 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.47 (s, 2H), 8.42 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 3.69−3.81 (m, 4H), 2.80−2.92 (m, 4H), 2.03−2.17 (m, 8H). ^{13}C NMR (100 MHz, tetrachlorethane-d_2): δ 160.6, 146.6, 135.2, 130.3, 129.5, 128.4, 124.1, 122.4, 118.0, 117.6, 114.7, 52.6, 25.7. MS (EI, 70 eV) *m/z*: 530.1 (100) [M$^+$], 531.2 (35.9) [M$^+$ + H] (calcd 530.14). HRMS (EI): calcd for $C_{32}H_{22}N_2O_6$ 530.1479, found 530.1480. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 709 (33 500), 435 (13 380), 318 (22 420), 276 (18 670), 252 (37 330). Fluorescence (CH_2Cl_2): λ_{max} = 744 nm, fluorescence quantum yield Φ_f = 0.18.

***N,N′*-Di(4-dodecylphenyl)-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisimide (4b).** A mixture of 33.0 mg (0.062 mmol) of **5**, 78.0 mg (0.30 mmol) of 4-dodecylaniline, 20.0 mg (0.10 mmol) of Zn(OAc)$_2$, and 5 mL of quinoline was heated under stirring at 180 °C for 18 h under Ar. A 7 mL portion of 15% HCl was poured into the cooled mixture under stirring. The resulting precipitate was separated by filtration, washed with 40 mL of water, dried at 40 °C/10^{-3} mbar, and purified by column chromatography (CH_2Cl_2/CH_3OH (50/1, v/v)) to yield 28 mg (44%) of **4b**. Mp: 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.48 (s, 2H), 8.39 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.4 Hz, 4H), 7.25 (d, J = 8.4 Hz, 4H), 3.65−3.80 (m, 4H), 2.75−2.91 (m, 4H), 2.68−2.72 (m, 4H), 1.90−2.10 (m, 4H), 1.66−1.73 (m, 4H), 1.20−1.45 (m, 40H), 0.80−0.95 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.3, 146.6, 143.4, 134.6, 133.1, 130.2, 129.4, 128.3, 126.9, 123.9, 122.5, 121.9, 121.1, 119.3, 118.3, 52.2, 35.8, 31.9, 31.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 25.8, 22.7, 14.1. MS (EI, 70 eV) *m/z*: 1016.5 (100) [M$^+$], 1017.4 (75.2) [M$^+$ + H]. HRMS (EI): calcd for $C_{68}H_{80}N_4O_4$ 1016.610, found 1016.604. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 706 (45 760), 435 (17 950), 315 (28 400), 245 (63 570). Fluorescence (CH_2Cl_2): λ_{max} = 745 nm, fluorescence quantum yield Φ_f = 0.20. Anal. Calcd for $C_{68}H_{80}N_4O_4 \cdot H_2O$ (1035): C, 78.85; H, 7.77; N, 5.40. Found: C, 79.21; H, 8.06; N, 5.38.

***N,N′*-Di(3,4,5-tridodecyloxyphenyl)-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisimide (4c).** A mixture of 100 mg (0.188 mmol) of **5**, 518 mg (0.80 mmol) of 3,4,5-tridodecyloxyaniline, 50.0 mg (0.25 mmol) of Zn(OAc)$_2$, and 10 mL of quinoline was heated under stirring at 180 °C for 24 h under Ar. A 45 mL portion of 15% HCl was poured into the cooled mixture under stirring. The resulting precipitate was separated by filtration, washed with 20 mL of water and 10 mL of methanol, dried at 40 °C/10^{-1} mbar, and purified by column chromatography (THF/hexane (1/2, v/v)) to yield 111 mg (33%) of **4c**. Mp: 93−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.45 (s, 2H), 8.40 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 6.59 (s, 4H), 4.03−4.06 (m, 4H), 3.94−3.97 (m, 8H), 3.65−3.75 (m, 4H), 2.73−2.81 (m, 4H), 1.95−2.04 (m, 8H), 1.75−2.04 (m, 12H), 1.20−1.52 (m, 108H), 0.84−0.90 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.3, 153.6, 146.7, 138.2, 130.6, 130.3, 124.2, 122.6, 121.2, 119.4, 118.4, 106.9, 73.5, 69.1, 52.3, 31.9, 30.4, 29.8, 29.7, 29.7, 29.4, 29.4, 26.2, 26.1, 25.8, 22.7, 14.1. MS (MALDI-TOF) *m/z*: 1787.5 [M$^+$], 1788.5 [M$^+$ + H] (calcd 1787.7). UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 707 (44 800), 436 (18 300), 346 (28 600), 271 (38 600), 245 (73 700). Fluorescence (CH_2Cl_2): λ_{max} = 741 nm, fluorescence quantum yield Φ_f = 0.34.

***N*-Cyclohexyl-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (6).** A mixture of 50.0 mg (0.072 mmol) of **4a**, 200 mg (3.60 mmol) of KOH, 0.5 mL of water, and 3 mL of *i*-PrOH was brought to reflux. The mixture was stirred for 2.75 h and poured under stirring into 10 mL of AcOH. The resulting green precipitate was extracted with 40 mL of methylene chloride, washed with water, dried over $MgSO_4$, and concentrated by rotary evaporation. Column chromatography on silica gel (chloroform/acetone/hexane (10/1/9, v/v/v)) afforded 28 mg of the starting material **4a** and 17 mg (88%) of **6**. Mp: 300−302 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.44 (s, 1H), 8.36 (s, 1H) 8.34 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.1 Hz, 1H) 7.61 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 5.03−5.10 (m, 1H), 3.62−3.79 (m, 4H), 2.71−2.90 (m, 4H), 2.55−2.64 (m, 2H), 1.90−2.10 (m, 10H), 1.70−1.85 (m, 3H), 1.35−1.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.4, 161.3, 160.8, 147.1, 146.2, 135.8, 133.4, 130.2, 130.2, 128.7, 126.4, 124.7, 124.3, 123.5, 123.1, 122.3, 122.1, 120.9, 120.4, 119.6, 117.1, 116.8, 114.2, 53.9, 52.4, 52.3, 29.2, 26.6, 25.8, 25.8, 25.5. MS (EI, 70 eV) *m/z*: 611.2 (100) [M$^+$], 612.2 (41.4) [M$^+$ + H] (calcd 611.2). HRMS (EI): calcd for $C_{38}H_{33}N_3O_5$ 611.2420, found 611.2420. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 708 (35 870), 436 (14 520), 317 (24 130), 275 (21 900), 250 (45 000). Fluorescence (CH_2Cl_2): λ_{max} = 746 nm, fluorescence quantum yield Φ_f = 0.14. Anal. Calcd for $C_{38}H_{33}N_3O_5$: C, 74.53; H, 5.39; N, 6.86. Found: C, 74.36; H, 5.54; N, 6.87.

***N,N′*-Dicyclohexyl-1-bromo-7-pyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisimide (7).** In a three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer was stirred a mixture of 95.0 mg (0.133 mmol) of *1,7*-**3** and 4.30 g (59.7 mol) of pyrrolidine under Ar for 24 h at 46 °C (internal). The mixture was poured under stirring into 10 mL of 10% HCl. The resulting green precipitate was separated by filtration, washed with water (2 × 10 mL) and 10 mL of methanol, dried at 60 °C/10^{-3} mbar, and purified by column chromatography (CH_2Cl_2) to yield 26.0 mg (28%) of **7** as a green powder. Mp > 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.52 (d, J = 8.3 Hz, 1H), 8.87 (s, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.51 (s, 1H), 8.46 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 4.98−5.10 (m, 2H), 3.69−3.75 (m, 2H), 2.75−2.85 (m, 2H), 2.50−2.64 (m, 4H), 1.98−2.18 (m, 4H), 1.89−1.93 (m, 4H), 1.72−1.77 (m, 6H), 1.30−1.47 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 164.2, 163.9, 163.2, 148.4, 137.5, 134.6, 134.2, 131.5, 130.5, 129.7, 129.5, 128.0, 127.3, 125.5, 123.9, 123.4, 122.5, 121.8, 121.4, 118.9, 117.3, 114.9, 54.0, 53.9, 52.7, 29.2, 29.1, 26.6, 25.9, 25.5. MS (MALDI-TOF) *m/z*: 701.2 [M$^+$] (calcd 701.2). UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 656 (27 300), 437 (15 000), 296 (25 900). Fluorescence (CH_2Cl_2): λ_{max} = 734 nm, fluorescence quantum yield Φ_f = 0.19. Anal. Calcd for $C_{40}H_{36}BrN_3O_4$: C, 68.38; H, 5.16; N, 5.98. Found: C, 68.15; H, 5.16; N, 6.06.

***N,N′*-Dicyclohexyl-1-cyano-7-pyrrolidinylperylene-3,4:9,10-tetracarboxylic Acid Bisimide (8).** *N,N′*-Dicyclohexyl-1-bromo-7-pyrrolidinylperylene bisimide **7** (100 mg, 0.142 mmol), zinc cyanide (67.0 mg, 0.568 mmol), 1,1′-bis(diphenylphosphino)ferrocene (5.0 mg, 0.01 mmol), and tris(dibenzylideneacetone)dipalladium(0) (10.0 mg, 0.010 mmol) were refluxed in 6 mL of dioxane for 20 h under argon. The reaction mixture was diluted with 20 mL of chloroform and filtered through Celite, and the solvent was removed on a rotary evaporator. The crude product was purified by silica gel column chromatography (with $CHCl_3$ as eluent) to yield 77 mg (84%) of **8**. Mp > 350 °C. $R_f = 0.19$ ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.50 (d, $J = 8.3$ Hz, 1H), 8.85 (s, 1H), 8.74 (d, $J = 8.1$ Hz, 1H), 8.56 (s, 1H), 8.55 (d, $J = 7.7$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 5.01−5.07 (m, 2H), 3.70−3.90 (m, 2H), 2.62−2.82 (m, 2H), 2.54−2.60 (m, 4H), 2.10−2.20 (m, 2H), 2.00−2.10 (m, 2H), 1.90−1.93 (m, 4H), 1.73−1.76 (m, 6H), 1.32−1.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 164.2, 164.0, 163.3, 149.8, 144.2, 138.5, 136.1, 135.8, 133.8, 132.9, 130.4, 129.9, 129.3, 128.5, 126.6, 125.1, 124.6, 122.9, 122.5, 122.0, 120.7, 118.9, 117.8, 103.9, 54.6, 54.4, 53.4, 29.6, 29.4, 26.9, 26.2, 25.8. MS (EI, 70 eV) *m/z*: 648.2 (32.4) [M$^+$], 649.2 (16.5) [M$^+$ + H] (calcd 648.3). HRMS (EI) calcd for $C_{41}H_{36}N_4O_4$ 648.2739, found 648.2733. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}) = 684 (27 600), 476 (6600), 425 (15 800), 300 (23 100). Fluorescence (CH_2Cl_2): $\lambda_{max} = 754$ nm, fluorescence quantum yield $\Phi_f = 0.10$. Anal. Calcd for $C_{41}H_{36}N_4O_4$: C, 75.90; H, 5.59; N, 8.64. Found: C, 75.27; H, 5.75; N, 8.54.

Crystal Structure Determination. All data were collected from shock-cooled crystals on a Bruker Smart-Apex diffractometer at 173 K[27] (graphite-monochromated Mo Kα radiation, $\lambda = 71.073$ pm) in the range $\theta_{min} = 2.50°$ to $\theta_{max} = 25.05°$. A total of 32 463 reflections were collected, and 10 628 unique reflections ($|I| > 2\sigma\ |I|$) were solved by direct methods and refined on F^2 using the full-matrix least-squares methods of SHELXL 97.[28] An empirical absorption correction was employed. Hydrogen atoms were calculated and included in the refinement. Non-hydrogen atoms were assigned with anisotropic displacement parameters, converging to a final R factor of 0.0558 and a weighted R factor of 0.1515 ($w = 1/[\sigma^2(F_o^2) + (0.0950P)2 + 5.1855P]$, where $P = (F_o^2 + 2F_c^2)/3$).

Crystallographic data of 1,7-dibromoperylene bisimide *1,7*-**3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nr. 242920).

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Supporting Information Available: X-ray crystallographic data of 1,7-dibromoperylene bisimide *1,7*-**3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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