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Synthesis of Regioisomerically Pure 1,7-Dibromoperylene-3,4,9,10-tetracarboxylic Acid Derivatives

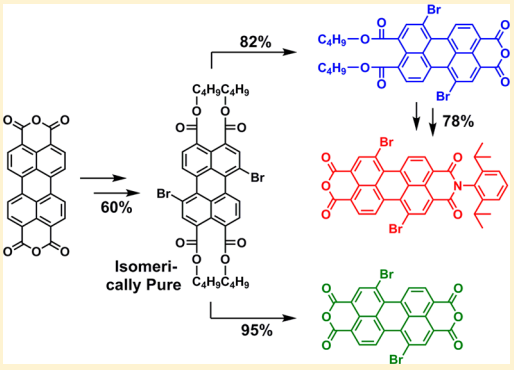
Sanchita Sengupta,[†,‡,∥] Rajeev K. Dubey,[†,‡] Rob W. M. Hoek,[†] Sjoerd P. P. van Eeden,[†] D. Deniz Gunbaş,[†,‡] Ferdinand C. Grozema,[†,‡,§] Ernst J. R. Sudhölter,[†] and Wolter F. Jager*[,†,§]

[†]Laboratory of Organic Materials & Interfaces and [‡]Laboratory of Optoelectronic Materials, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628BL Delft, The Netherlands

[§]BioSolar Cells, P.O. Box 98, 6700 AB Wageningen, The Netherlands

Supporting Information

ABSTRACT: The perylene derivative 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutylester has been obtained in *regioisomerically pure* form, by employing a highly efficient, scalable, and robust synthesis starting from commercially available perylene-3,4,9,10-tetracarboxylic bisanhydride. Subsequently, this compound is utilized for the synthesis of extremely valuable and versatile regioisomerically pure intermediates, namely, 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dibutylester monoanhydride, 1,7-dibromoperylene-3,4,9,10-tetracarboxylic bisanhydride, and 1,7-dibromoperylene monoimid monoanhydride. These compounds possess at least one anhydride functionality in addition to the 1,7 bromo substituents and thus allow for a virtually limitless attachment of substituents both at the "peri" and the "bay" positions. The intermediate 1,7-dibromoperylene monoimide monoanhydride is of special interest as it provides access to unsymmetrically imide-substituted 1,7-dibromoperylene derivatives, which are not accessible by previously known procedures. Finally, substitution of the 1,7 bromine atoms in the bay area by phenoxy groups, which is a generally applied reaction for 1,7-dibromoperylene bisimides, was proven to be equally effective for a 1,7-dibromoperylene tetraester and a 1,7-dibromoperylene diester monoimid.



INTRODUCTION

Perylene bisimides (PBIs) form a class of highly valuable organic dyes, which have become an integrated part of both academic and industrial research. Alongside, these dyes have also found numerous real and potential applications mainly because of their outstanding physical properties, such as chemical robustness, photo- and thermal stability, and excellent optical and electronic properties. Over the course of time, these dyes have been applied as industrial colorants, fluorescent sensors, and *n*-type semiconductors in the burgeoning field of organic electronics and photovoltaics.[1]

In addition to the archetypal perylene bisimides, a number of perylene-3,4,9,10-tetracarboxylic acid derivatives have been developed. These derivatives have altered optical and electrochemical properties, while maintaining excellent stability, good solubility, and high fluorescence quantum yields. Representative examples, **A1**,[2] **B1**,[3] **C1**, and **D1**,[2] are presented in Figure 1. The absorption and emission spectra of these compounds shift bathochromically, and the electron deficiency generally increases upon going from left to the right in Figure 1.

Structural modification of **A1**−**D1**, by the attachment of various functional groups, has been realized either at the 3,4,9,10-tetracarboxylic acid "peri" positions or at the 1,6,7,12-positions, which are generally referred to as the bay positions. Only in the latter case, further modifications in the optical and electrochemical properties may occur. This is the case because nodal planes close to the carboxylic acid functions make these compounds insensitive to the substituent changes at the carboxylic acid positions. For this reason, bay-brominated derivatives (i.e., **A2**−**D2**), in which the bromine atoms can participate in a large variety of substitution reactions, are highly valuable and versatile intermediates for the synthesis of bay-functionalized chromophores with tunable optoelectronic properties.

Bay-area substitution with two or four substituents, generally, starts with halogenation of perylene-3,4,9,10-tetracarboxylic bisanhydride (PBA), yielding 1,7-dibromo-[4] or 1,6,7,12-tetrachloro-PBA,[5] respectively. The resultant 1,7-dibromo-PBA, however, is obtained as a mixture of 1,7- and 1,6-isomers and, thus, bay-area-substituted compounds synthesized from this mixture are not isomerically pure.[6] In an alternative procedure, dibromoperylene bisimides have been prepared by the direct bromination of non-bay-substituted bisimides.[7] Regioisomeric mixtures were obtained in this case also. It has been demonstrated recently that the optical and electrochemical properties of 1,6- and 1,7-substituted PBIs can be

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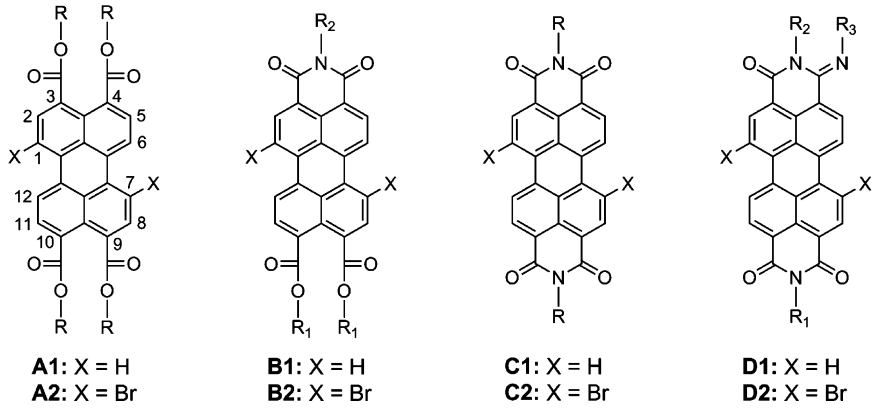
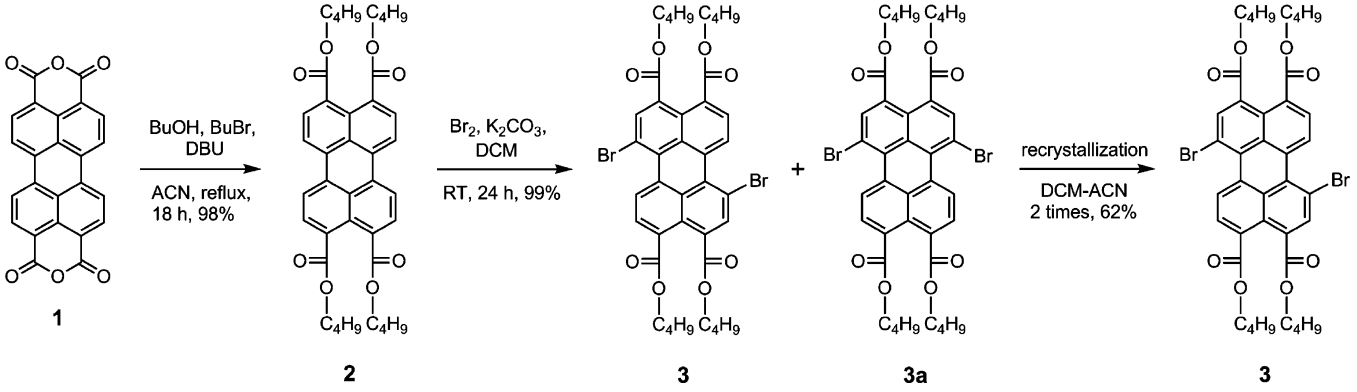
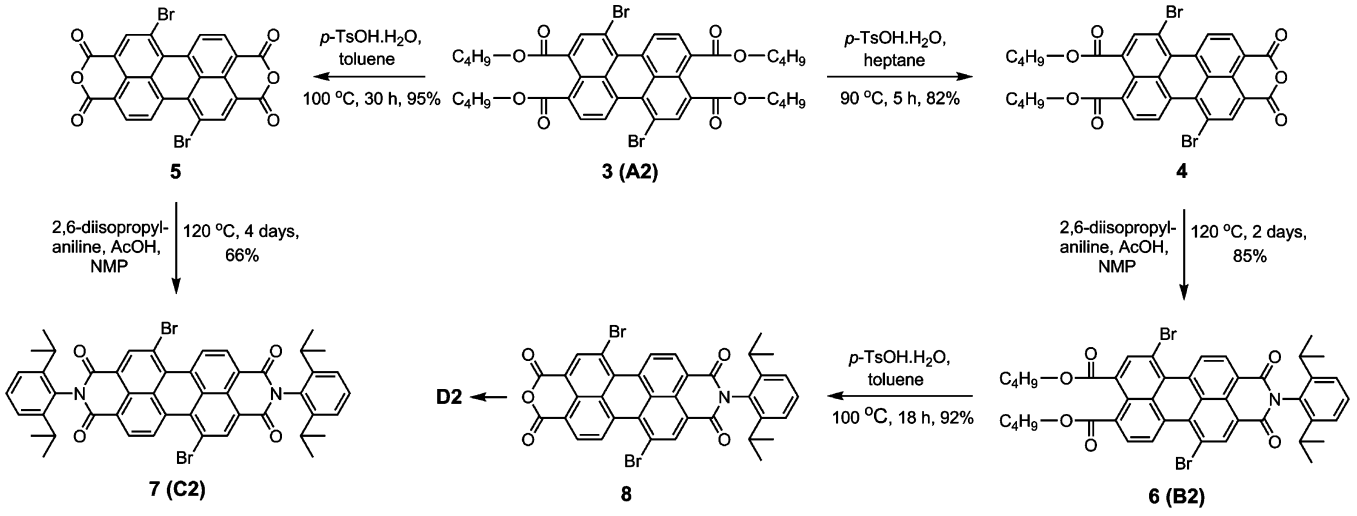


Figure 1. Perylene tetracarboxylic acid derivatives with altered optical and electronic properties.

Scheme 1. Synthesis of Regioisomerically Pure 1,7-Dibromoperylene-3,4,9,10-tetracarboxy Tetrabutylester 3 from PBA 1



Scheme 2. Synthesis of Regioisomerically Pure 1,7-Dibromo-Substituted Compounds 4−8 from 3



markedly different.[8] Therefore, isomeric purity of these compounds is highly relevant.

Similar to 1,7-dibromo-PBA and PBIs, the synthesis of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetraesters (PTEs) has also been reported.[9] PTEs have, so far, not been obtained in isomerically pure form. For specific derivatives synthesized from mixtures of 1,7- and 1,6-isomers of dibromo-PBA and PTEs, improved isomeric purity and, eventually, pure 1,7-substituted products have been obtained by using various techniques, such as repetitive recrystallization, chromatography, or separation based on solubility difference.[6,8,9,10a] However, these methods are generally not suitable for large-scale synthesis of regioisomerically pure derivatives because they are cumbersome and less efficient. In addition, these are not versatile methods because they are applicable to specific compounds only and sensitive to the changes in the structure of these molecule. Therefore, it would be highly advantageous to start the synthesis of bay-area-substituted perylenes from isomerically pure 1,7-dibromo-PBA, PBIs, or PTEs in the first place.

We present, herein, the very first synthesis of regioisomerically pure 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid

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derivatives **3**–**8**. The synthesized compounds are excellent starting materials for the synthesis of a large range of regioisomerically pure perylene derivatives. In particular, compounds **4**, **5**, and **8**, which have at least one anhydride functionality in addition to the 1,7 bromo substituents, allow for a virtually unlimited attachment of substituents at both the peri and the bay positions. The reported reactions are suitable for multigram-scale syntheses of various isomerically pure 1,7-dibromoperylene derivatives because of their high yields and convenient purification processes. With the synthesis of the bay-area-substituted compounds **9** and **10**, we have demonstrated that the substitution of the bay-area bromines, which is generally applied for 1,7-dibromo-PBIs like **7**, can be accomplished for a 1,7-dibromoperylene tetraester (**3**) and a 1,7-dibromoperylene diester monoimid (**6**), as well.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of all reported compounds (**3**–**8**) begins with the commercially available perylene-3,4,9,10-tetracarboxylic bisanhydride (**1**) and is outlined in Schemes 1 and 2. All the compounds were prepared in 2–5 steps from **1** in overall yields between 38% and 60%.

In the first step, perylene-3,4,9,10-tetrabutylester (**2**) has been synthesized from **1** in high yield by following a known procedure.[2] The dibromination of **2**, in DCM at room temperature, was highly efficient under very mild conditions.[9] From the resulting mixture of the dibromides **3** and **3a**, generally obtained in a 4:1 ratio,[11] the desired 1,7-isomer **3** was obtained in the pure form by crystallization from an acetonitrile/dichloromethane mixture. The first crystallization yielded a mixture of **3** and **3a** in a 10:1 ratio. The purification process was monitored by ^{1}H NMR spectroscopy. Figure 2

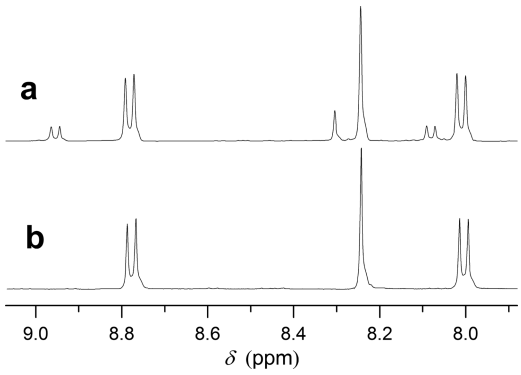

Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectra: (a) 4:1 regioisomeric mixture of **3** and **3a** obtained after the reaction and (b) **3** after purification by recrystallization.

shows ^{1}H NMR spectra of the crude product, and pure compound **3** obtained after a second crystallization. The overall yield of this reaction, forming **3** out of **1**, is around 60%. Higher yields, approaching the 80% of **3** present in the initial mixture, can be obtained, by further workup of the mixture of **3** and **3a** that is obtained after the first sequence of crystallizations. However, the 62% reported here is routinely obtained by a single sequence of crystallizations. It is important to note that the large-scale synthesis of compound **3** can be performed quite easily because of the remarkably convenient reaction conditions and facile purification procedures. Typically, the bromination of **2** is performed on a 10 g scale, and from the resulting 12.3 g of crude bromoperylene, **3** is obtained in multigram batches.

The conversion of **3** to **4** was achieved by an acid-catalyzed removal of two ester moieties in heptane at 90 °C and turned out to be highly efficient.[12] The decreased solubility of **4**, as compared to **3**, explains the selectively of this reaction toward yielding **4**. The yield of **4** is significantly reduced at temperatures higher than 90 °C and solvents more polar than heptane because of the enhanced formation of the side product **5**.

The conversion of **3** to the corresponding bisanhydride **5** required an excess of *p*-TsOH·H_2O, a higher temperature, and a better solvent to keep the primary reaction product **4** in solution. Treatment of **3** with 5 equiv of *p*-TsOH·H_2O in toluene at 100 °C gave the best results, yielding **5** in 95% yield. Compound **5** is a valuable and highly versatile synthon that provides direct access to many perylene derivatives, using the well-established methods developed for perylene bisanhydride **1**.[13] It should be noted that direct bromination of **1** yields **5**, along with its 1,6-isomer and the 1,6,7-tribromide as an inseparable mixture. Therefore, our proposed synthesis is the first method for obtaining isomerically pure **5** in practical quantities. The imidization of the anhydrides **4** and **5**, with 2,6 diisopropylaniline, was performed in NMP and acetic acid,[10a] and overall yields of **6** and **7** were 85% and 66%, respectively.[14] Clear enough, the ester functionalities in **4**, as well as the bromine atoms in the bay area, were stable under these harsh reaction conditions.

In order to access compound **8**, a heretofore unknown compound that provides easy access to unsymmetric 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimides and chromophore **D2**, we treated **6** with 5 equiv of *p*-TsOH·H_2O in excess toluene. The reaction yielded **8** in 92% yield. It should be noticed that compound **8** cannot be synthesized directly from 1,7-dibromoperylene bisimides (like **7**), by the cleavage of a single imide functionality using concentrated KOH.[15] This is mainly because the harsh reaction conditions will affect the 1,7-dibromo substituents.

For attaching substituents to 1,7-dibromo-PBAs, like **7**, various methods, such as Suzuki[16] and Sonogashira[17] couplings, and nucleophilic aromatic substitution reactions, mostly with sulfides,[18] cyclic amines,[19] aliphatic alcohols,[20] and phenols,[4a,8c,21] have been reported. For the tetraester compound **3**, in contrast, only a limited number of bay-area substitutions have been reported, mostly with highly fluorinated substituents,[9,22] and generally with low yields.[23] Bay-area substitution on a regioisomeric mixture of monoimid diester compounds has been reported once.[24] Here, we demonstrate the value of **6** and **3** as a synthon for bay-area substitution by the synthesis of **9** and **10**, using a phenol coupling (Scheme 3).

Similar to perylene bisimides, the coupling reaction of compound **6** with 4-methoxyphenol proceeded smoothly at 95 °C in toluene to afford product **9** in 85% yield. This clearly indicates that compound **6** also has a high reactivity toward nucleophilic substitution reactions. However, the reaction of compound **3** with 4-methoxyphenol did not proceed under these mild reaction conditions. Eventually, the reaction was successfully carried out at 130 °C in DMF to give compound **10** in 88% yield.[25] The observed reluctance of compound **3** for phenoxy substitution can be attributed to the decreased electron deficiency, which results in a decreased reactivity of **3** compared to 1,7-dibromoperylene bisimides. Purification of compounds **9** and **10** has been achieved by silica gel column

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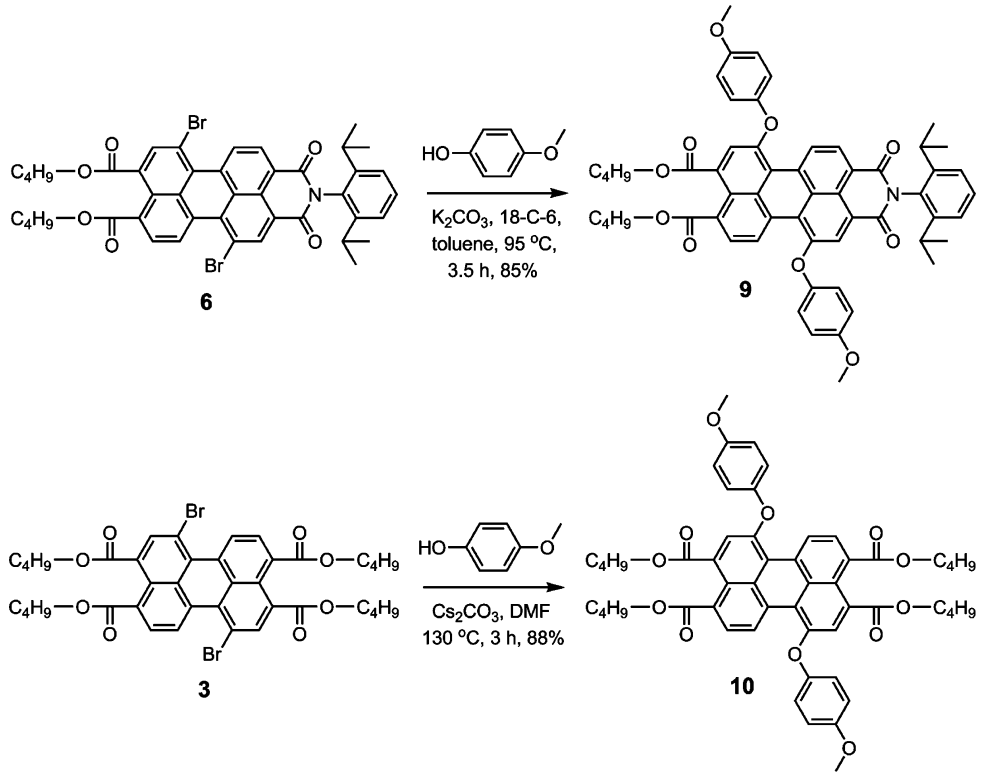
Scheme 3. Synthesis of Bay-Functionalized Derivatives 9 and 10



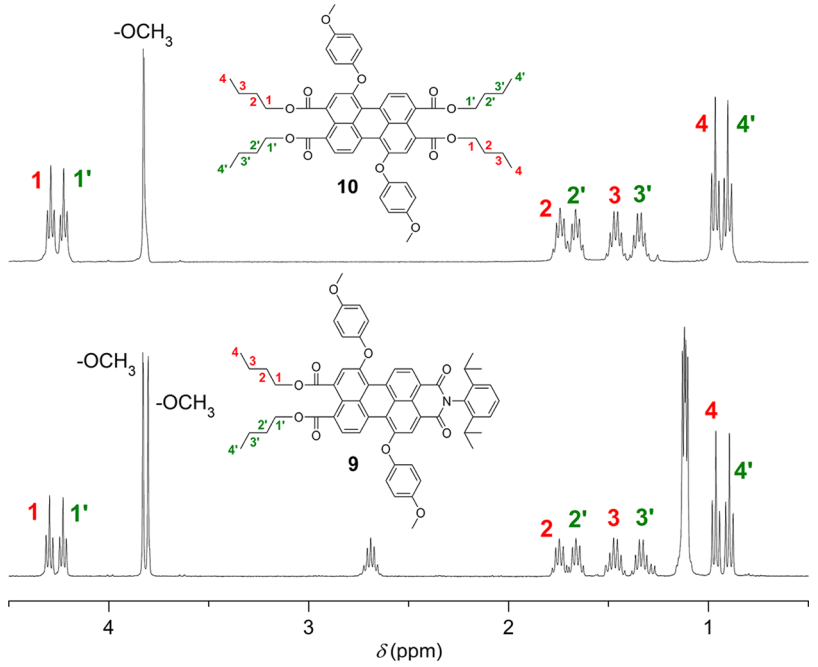


Figure 3. ^{1}H NMR spectra (aliphatic region) of compounds **10** and **9** in $CDCl_3$.

chromatography. Recrystallization from ethanol, a solvent in which the starting compounds, unlike the products, are highly soluble, was equally successful and is recommended for synthesis on a larger scale.

The ^{1}H NMR spectra of compounds **9** and **10** are depicted in Figure 3. The spectrum of **10** reveals the C_2 symmetry of this molecule. Because of the ring current effect of the aromatic bay-area substituents, all methylene and methyl protons of the distinct butyl tails are split into separate signals. Such a splitting is barely visible in the ^{1}H NMR spectrum of the analogous bromo-substituted compound **3**. The ^{1}H NMR spectrum of **9** provides excellent proof of the 1,7-substitution and the subsequent lack of symmetry in this compound. Just like for **10**, the butyl protons are split into separate signals. But now, even the methoxyphenol groups are inequivalent and their signals are split as well.

Photophysical Studies. The absorption and emission spectra of compounds **3**, **6**, and **7** in chloroform are shown in

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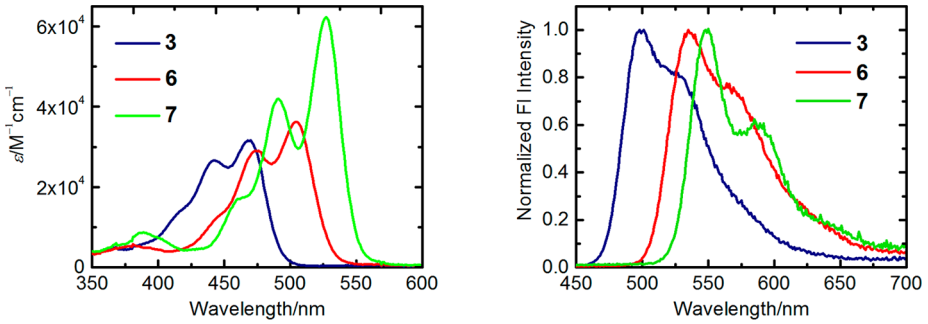

Figure 4. UV/vis absorption (left) and normalized fluorescence spectra (right) of compounds **3**, **6**, and **7** in chloroform.

Table 1. Optical Properties of Compounds 3, 6, and 7 in Chloroform and Their First Reduction Potentials in Dichloromethane (vs Ag/Ag$^+$)

compound	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_f	τ_f (ns)	$E_{1/2\ red}$ (V)
3	470	31600	498	0.26	1.78	−1.03
6	504	36200	535	0.91	4.75	−0.66
7	527	62100	548	0.79	4.36	−0.46
9	521	30600	564	0.55	2.77	
10	478	25500	522	0.91	4.47	

Figure 4, and the relevant optical data of these compounds are summarized in Table 1. The relative differences in their optical properties are clearly evident. All three compounds exhibit well-defined S_0−S_1 absorption bands in the visible region, which is a characteristic feature of the aromatic perylene core. As we move from compound **3** to **6** to **7**, the characteristic absorption band is shifted bathochromically. Simultaneously, the extinction coefficients ε increase. A similar bathochromic shift was also observed in their emission profile. The absorption and emission spectra of the diphenoxy-functionalized compounds, **9** and **10**, were bathochromically shifted compared to their corresponding dibromo-functionalized analogues (Table 1). This observation, which can be explained by the electron-donating character of the phenoxy substituents, verifies the importance of bay functionalization to tune optoelectronic properties of these chromophores.

The relative difference in the electron-accepting behavior of the chromophores **3**, **6**, and **7** was investigated by cyclic voltammetry in CH_2Cl_2. The obtained first reduction potential values are listed in Table 1, and the cyclic voltammograms are shown in Figure S1 (Supporting Information). As can be seen, PBI **7** is the most electron-deficient compound in the series, because of the presence of two imide groups that are more electron-withdrawing than the ester groups. For the same reason, PTE **3** exhibits the highest value of the first reduction potential. The exposed differences in the optical and electrochemical properties of the synthesized compounds underline the importance of developing practical synthetic routes for the preparation of these compounds.

CONCLUSIONS

We have devised a new route for the synthesis of the *isomerically pure* 1,7-dibrominated synthons **3**−**8**. These newly synthesized compounds are exellent starting materials for the synthesis of a large variety of bay-area-substituted compounds with excellent control over optical and electrochemical properties. In addition, the unsymmetrically substituted dibromoperylene derivatives **4** and **8** are excellent synthons for the preparation of unsymmetrically substituted perylenes bearing a variety of bay-area substituents. With the synthesis of compounds **9** and **10**, we have demonstrated that substitution of the bromine atoms at the bay area is efficient for all perylene-3,4,9,10-tetracarboxylic acid derivatives reported in this paper. The reported reactions are suitable for multigram-scale syntheses of the isomerically pure derivatives because of their high efficiencies and convenient purification processes. In our current research, these reactions are employed for the synthesis of light-harvesting antenna systems.

EXPERIMENTAL SECTION

Materials. All the reagents utilized were used as received from the manufacturer, unless otherwise stated. The DMF used in the synthesis was of anhydrous grade. Toluene was dried over sodium under an argon atmosphere prior to use. The purification of the products was performed by column chromatography (silica gel 60, mesh size 0.063−0.200 mm).

Instrumentation and Characterization. The NMR spectra were recorded with a 400 MHz pulsed Fourier transform NMR spectrometer in $CDCl_3$ at room temperature. The chemical shifts are quoted relative to $CDCl_3$ [δ = 7.26 ppm (^{1}H, singlet); 77.00 (^{13}C, triplet)]. δ values are given in ppm and J values in Hz. The ^{1}H NMR spectrum of compound **5** was measured in D_2SO_4.[6] High-resolution mass spectra were recorded with a MicroTOF spectrometer using the positive electrospray ionization mode (ESI). The samples were prepared in methanol, and 1 M sodium formate solution was used as a calibrant. Electrochemical behavior of the compounds was studied by cyclic voltammetry in a three-electrode single-compartment cell consisting of a platinum electrode as the working electrode, Ag wire as the reference electrode, and a Pt wire as the counter electrode at a scan rate of 0.5 V/s. The cell was connected to the computer-controlled potentiostat. Predried CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate was used as solvent. The measurements were done under a continuous flow of nitrogen. The concentration of the prepared samples was ca. 0.5 mM.

All the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded with a double beam UV/vis spectrophotometer. Emission spectra were corrected for the wavelength response of the detection system. Fluorescence quantum yields were determined by the comparative method using perylene-3,4,9,10-tetracarboxylictetramethyl ester (Φ_f = 0.95 in CH_2Cl_2) as a reference.[26] Optical densities at the excitation wavelengths were maintained at around 0.1 to avoid reabsorption.

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Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxy tetrabutylester (3). In a 250 mL round-bottom flask, perylene tetrabutylester **2** (10 g, 15.32 mmol) and K_2CO_3 (5 g, 36.18 mmol) were taken, and CH_2Cl_2 (125 mL) was added. To this mixture, subsequently, bromine (10 mL, 193.98 mmol) was added dropwise. The reaction mixture was stirred for 24 h at room temperature. Thereafter, a saturated aqueous solution of $NaHSO_3$ was added dropwise to the reaction mixture with stirring. The organic layer was washed with several portions of water and dried over Na_2SO_4. The solvent was removed by rotary evaporation to afford the crude product (12.27 g, ca. 99%) consisting of a mixture of 1,7- and 1,6-dibromo isomers. Isolation of regioisomerically pure **3** was achieved by a double crystallization from dichloromethane/acetonitrile.

In a typical procedure, the crude regioisomeric mixture (4 g) was taken in a 1 L round-bottom flask and dissolved in a minimum amount of dichloromethane (ca. 40 mL). Subsequently, acetonitrile (ca. 360 mL) was added to the solution. The flask was left open in the hood, and crystals were isolated after 2−3 days. Typically, a 10:1 mixture of **3** and **3a** is obtained after the first crystallization, while pure **3** is obtained in subsequent crystallizations. The final yield of **3** was 2.50 g (62%). mp 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (d, J = 8.0 Hz, 2H), 8.29 (s, 2H), 8.09 (d, J = 8.0 Hz, 2H), 4.34 (t, J = 6.8 Hz, 8H), 1.80−1.77 (m, 8H), 1.54−1.46 (m, 8H), 1.01−0.98 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 19.2, 30.1, 65. 6, 65. 8, 118.6, 126.4, 127.5, 128.9, 130.3, 130.4, 131.0, 132.0, 136.6, 167.1, 167.9 ppm. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{40}H_{42}Br_2O_8$, 833.1139; found, 833.1110.

Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxy monoanhydride Dibutylester (4). Regioisomerically pure compound **3** (1 g, 1.23 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (305 mg, 1.60 mmol) were taken in 3 mL of *n*-heptane. The reaction mixture was stirred at 90 °C for 5 h. After some time, the product **4** started to precipitate from the reaction mixture. After 5 h, the reaction mixture was cooled to room temperature and the product was filtered off and washed with a few portions of methanol and water. Subsequently, the dried orange precipitate was taken in methanol (200 mL) and refluxed for 2 h. It was cooled to room temperature and filtered to remove the starting compound. The residue was the monoanhydride compound **4**, whereas the starting material **3** remains soluble in methanol. Finally, the dried residue was dissolved in a limited amount of dichloromethane and filtered to remove insoluble bisanhydride **5**. The solvent was evaporated to afford the pure product (690 mg, 82%). Around 100 mg of starting compound **3** was recovered. Additional purification by column chromatography, using chloroform, is recommended to get rid of traces of bisanhydride **5**. mp 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (d, J = 8.0 Hz, 1H), 9.24 (d, J = 8.0 Hz, 1H), 8.90 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.35 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 4.38−4.34 (m, 4H), 1.84−1.76 (m, 4H), 1.53−1.47 (m, 4H), 1.03−0.98 ppm (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 18.88, 18.91, 29.3, 30.22, 30.25, 65.6, 65.8, 117.5, 117.6, 118.9, 120.8, 126.6, 127.9, 128.3, 128.6, 128.7, 128.8, 129.6, 129.9, 131.7, 131.8, 132.2, 134.8, 135.2, 136.5, 139.3, 158.8, 159.1, 166.4, 167.2 ppm. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{32}H_{24}Br_2O_7$, 702.9781; found, 702.9763.

Synthesis of 1,7-Dibromoperylene-3,4,9,10-tetracarboxylic bisanhydride (5). A mixture of regioisomerically pure compound **3** (2.0 g, 2.47 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (2.4 g, 12.35 mmol), in toluene (70 mL), was stirred for 30 h at 100 °C. After being cooled to room temperature, the reaction mixture was filtered, and the residue was washed with methanol and water several times. Thereafter, the dried precipitate was taken in chloroform (150 mL) and refluxed for a few hours. It was cooled to room temperature and filtered to remove the soluble monoanhydride (**4**). The residue was then washed with $CHCl_3$ and dried to obtain the pure product **5** (1.3 g, 95%). mp > 350 °C. ^{1}H NMR (400 MHz, D_2SO_4): δ = 9.68 (d, J = 8.4 Hz, 2H), 9.01 (s, 2H), 8.79 ppm (d, J = 8.4 Hz, 2H). ^{13}C NMR spectra could not be measured because of its low solubility.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (6). A 25 mL round-bottom flask was charged with dibromoperylene-diester monoanhydride **4** (0.54 g, 0.79 mmol), 2,6-diisopropylaniline (0.31 g, 1.75 mmol), acetic acid (0.25 mL, 4.36 mmol), and NMP (5 mL). The reaction mixture was stirred at 120 °C for 2 days under an Ar atmosphere. After being cooled to room temperature, the reaction mixture was poured in water to precipitate the crude product. The precipitate was filtered off and washed with several portions of water to remove NMP. The precipiteate was dried and chromatographed on silica-60, eluting with CH_2Cl_2, to afford the desired product **6** (0.57 g, 85%). mp 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.27 (d, J = 7.9 Hz, 1H), 9.24 (d, J = 8.0 Hz, 1H), 8.95 (s, 1H), 8.73 (d, J = 8.1 Hz, 1H), 8.36 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 2H), 4.39−4.35 (m, 4H), 2.77−2.71 (m, 2H), 1.85−1.77 (m, 4H), 1.53−1.47 (m, 4H), 1.19 (s, 6H), 1.17 (s, 6H), 1.01 ppm (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 167.1, 163.4, 163.0, 145.8, 138.5, 137.1, 134.5, 134.1, 132.2, 132.1, 131.8, 131.1, 130.8, 130.7, 130.6, 130.0, 129.5, 129.3, 128.4, 128.3, 127.6, 127.1, 124.4, 122.3, 122.1, 120.5, 119.7, 66.2, 66.0, 30.8, 30.8, 29.4, 24.3, 19.5, 19.5, 14.0 ppm. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{44}H_{41}Br_2NO_6$, 862.1193; found, 862.1167. Anal. Calcd for $C_{44}H_{41}Br_2NO_6$: C, 62.94; H, 4.92; N, 1.67. Found: C, 62.83; H, 5.04; N, 1.71.

Synthesis of *N,N′*-Bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy Bisimide (7). Perylene bisimide **7** was prepared following the literature procedure.[10a] A 25 mL round-bottom flask was charged with dibromoperylene-bisanhydride **5** (0.30 g, 0.55 mmol), 2,6-diisopropylaniline (0.39 g, 2.20 mmol), acetic acid (0.18 mL, 3.15 mmol), and NMP (4 mL). The reaction mixture was stirred at 120 °C for 4 days under an Ar atmosphere. After being cooled to room temperature, the reaction mixture was poured in water to precipitate the crude product. The precipitate was filtered off and washed with several portions of water to remove NMP. The precipitate was dried and chromatographed on silica-60, eluting with CH_2Cl_2, to afford the desired bisimide **7** (0.31 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (d, J = 8.0 Hz, 2H), 9.02 (s, 2H), 8.80 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 6.8 Hz, 2H), 7.37 (d, J = 6.8 Hz, 4H), 2.74 (m, 4H), 1.20 (s, 12H), 1.18 ppm (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 162.5, 145.6, 138.5, 133.4, 133.3, 130.6, 130.1, 129.9, 129.6, 128.7, 127.7, 124.2, 123.2, 122.8, 121.0, 29.3, 24.02, 23.99 ppm.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (8). Compound **6** (100 mg, 0.12 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (114 mg, 0.60 mmol) were taken in 4 mL of toluene. The resulting mixture was stirred at 90 °C for 18 h. After being cooled to room temperature, the solvent was evaporated and the residue was dissolved in $CHCl_3$ (50 mL). The resulting solution was extracted with water a few times. The organic phase was collected, dried over Na_2SO_4, and evaporated. Thereafter, MeOH (75 mL) was added to the solid residue and refluxed for 2 h. After cooling down to room temperature, the precipitate was collected by filtration, dried, and dissolved in a minimum amount of refluxing $CHCl_3$. To this solution, MeOH was added to get the precipitate of the product. The precipitate was collected by filtration and dried to afford the pure product **8** (78 mg, 92%). mp > 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.58−9.55 (m, 2H), 9.02 (s, 1H), 8.98 (s, 1H), 8.80 (d, J = 8.0 Hz, 1H), 8.76 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 2.75−2.68 (m, 2H), 1.19 (s, 6H), 1.17 ppm (s, 6H). ^{13}C NMR could not be measured because of the limited solubility of **8** in $CDCl_3$. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{36}H_{23}Br_2NO_5$, 731.9835; found, 731.9797.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,7-di(4-methoxyphenoxy)perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (9). In dry glassware, a mixture of 4-methoxyphenol (40 mg, 0.32 mmol), K_2CO_3 (89 mg, 0.64 mmol), and 18-Crown-6 (339 mg, 1.28 mmol), in dry toluene (20 mL), was stirred for 45 min at room temperature under an argon atmosphere. Subsequently, compound **6** (90 mg, 0.11 mmol) was added. Thereafter, the reaction mixture was stirred for 3.5 h at 95 °C under an argon atmosphere. After being cooled to room temperature, the solvent was removed by rotary evaporation. The residue was washed with water, and then with cold

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MeOH to remove the unreacted 4-methoxyphenol, and dried. The crude product was purified by column chromatography (silica-60/$CHCl_3$) to afford the product **9** (84 mg, 85%). mp 208 °C. Alternatively, the compound can also be purified by recrystallization from EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (t, J = 8.0 Hz, 2H), 8.64 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 8.8 Hz, 4H), 6.97 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H), 4.32 (t, J = 6.8 Hz, 2H), 4.25 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 2.73−2.65 (m, 2H), 1.78−1.1 (m, 2H), 1.70−1.62 (m, 2H), 1.49−1.43 (m, 2H), 1.36−1.31 (m, 3H), 1.15−1.12 (m, 12H), 0.98 (t, J = 7.2 Hz, 3H), 0.91 ppm (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 167.1, 163.1, 162.6, 156.3, 156.1, 154.1, 154.0, 148.3, 147.9, 145.1, 133.8, 132.1, 131.6, 130.3, 130.2, 130.13, 130.08, 128.91, 128.88, 128.5, 127.9, 127.3, 125.1, 124.6, 124.0, 123.8, 123.4, 122.3, 122.2, 120.5, 120.3, 119.9, 114.9, 114.9, 65.0, 64.9, 55.2, 30.1, 29.9, 28.6, 23.4, 18.7, 18.6, 13.3, 13.2 ppm. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{58}H_{55}NO_{10}$, 948.3718; found, 948.3684. Anal. Calcd for $C_{58}H_{55}NO_{10}$: C, 75.22; H, 5.99; N, 1.51. Found: C, 74.98; H, 6.22; N, 1.57.

Synthesis of 1,7-Di(4-methoxyphenoxy)perylene-3,4,9,10-tetracarboxy Tetrabutylester (10). In a dry 25 mL round-bottom flask, weighed amounts of compound **3** (100 mg, 0.12 mmol), 4-methoxyphenol (61 mg, 0.49 mmol), and Cs_2CO_3 (240 mg, 0.74 mmol) were taken. Subsequently, anhydrous DMF (4 mL) was added. The reaction mixture was stirred at 130 °C for 3 h under an argon atmosphere. After being cooled to room temperature, CH_2Cl_2 (50 mL) was added to the reaction mixture and the resultant solution was extracted with water several times. The organic layer was collected, dried over Na_2SO_4, and evaporated. The crude product was chromatographed on silica-60, eluting with $CHCl_3$, to afford the desired product **10** (97 mg, 88%). mp 134 °C. Alternatively, the compound can be recrystallized from EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.10 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.68 (s, 2H), 7.04 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.8 Hz, 4H), 4.29 (t, J = 6.8 Hz, 4H), 4.23 (t, J = 6.8 Hz, 4H), 3.82 (s, 6H), 1.78−1.71 (m, 4H), 1.71−1.63 (m, 4H), 1.52−1.41 (m, 4H), 1.40−1.30 (m, 4H), 0.97 (t, J = 7.2 Hz, 6H), 0.90 ppm (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 167.8, 156.3, 152.9, 149.0, 131.2, 131.2, 129.2, 129.0, 127.1, 124.4, 123.4, 121.8, 120.5, 115.2, 65.3, 65.2, 55.7, 30.6, 30.4, 19.2, 19.1, 13.8, 13.7 ppm. MS (ESI-TOF): $[M + Na]^+$ Calculated for $C_{54}H_{56}O_{12}$, 919.3664; found, 919.3636. Anal. Calcd for $C_{54}H_{56}O_{12}$: C, 72.30; H, 6.29. Found: C, 72.23; H, 6.36.

■ ASSOCIATED CONTENT

Supporting Information

Cyclic voltammograms of compounds **3**, **6**, and **7** (Figure S1) and ^{1}H and ^{13}C NMR spectra of all synthesized compounds (Figures S2−S9). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: W.F.Jager@tudelft.nl.

Present Address

[‖]Interdisciplinary Center for Energy Research (ICER), Indian Institute of Science, Bangalore 560012, India.

Notes

The authors declare no competing financial interest.

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(14) The synthesis of the regioisomerically pure compound **7** has been reported in ref 10a. This synthesis yields **7** in a 36% yield from **1**, comparable to the 38% we have obtained. This synthesis, however, lacks the versatility of our method, because separation of the regioisomers is obtained in the last step and is substituent-specific.

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