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Novel Derivatives of 1,6,7,12-Tetrachloroperylene-3,4,9,10-Tetracarboxylic Acid: Synthesis, Electrochemical and Optical Properties

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Rajeev K. Dubey,*[a,b] Nick Westerveld,[a] Ernst J. R. Sudhölter,[a] Ferdinand C. Grozema,[b] and Wolter F. Jager*[a]

A family of novel unsymmetrical "peri"-substituted perylene-3,4,9,10-tetracarboxylic acid derivatives (**5–10**), with 1,6,7,12-tetrachloro-substitutents at the bay-positions, has been synthesized. Subsequently, their redox and optical properties have been explored with the intent of unveiling opto-electronic characteristics of these newly synthesized compounds. To synthesize these new compounds, pure 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic tetra-*n*-butylester (**4**) has been employed as the precursor and the structural modifications have been carried out exclusively at the "peri" positions in an efficient manner. The two synthons prepared in this work, 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic di-*n*-butylester monoanhydride (**5**) and 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic monoimide monoanhydride (**8**), are extremely valuable and versatile starting materials as they possess free anhydride functionality at the "peri" position in addition to the 1,6,7,12-tetrachloro-bay-substituents. Finally, the conventional methodology for the synthesis of 1,6,7,12-tetraphenoxy-bay-functionalized perylene bisimides and perylene bisbenzimidazoles has been modified to make it faster and more convenient.

Introduction

The chemistry of perylene-based dyes has been thoroughly investigated and developed in both the academic and the industrial domain.[1,2,3] Over the course of time, a number of important synthetic routes towards perylene-3,4,9,10-tetracarboxylic acid derivatives have been developed. Some representative classes of compounds that have been synthesized are presented in Figure 1, such as perylene-3,4,9,10-tetracarboxy tetraesters (**A1–A3**),[4,5,6,7] perylene-3,4,9,10-tetracarboxy monoimide diesters (**B1–B2**),[5,8,9] perylene-3,4,9,10-tetracarboxy bisimides (**C1–C3**),[1,3] and perylene-3,4,9,10-tetracarboxy bisbenzimidazoles (**D1–D3**).[8,10] In addition, methods to obtain perylene-3,4-dicarboxylic acid derivatives have also been reported.[11,12] These perylene derivatives have gained a lot of attention because of their inherently beneficial properties, e. g. chemical robustness, photo and thermal stability, strong absorption and emission in the visible region, as well as high electron affinities and charge carrier mobilities. These compounds have been extensively employed as the photo-functional materials for the construction of efficient and tunable electron donor–acceptor systems[13,14,15,16,17] and light-harvesting arrays.[18,19,20,21] These dyes have also been used in other photo-physical processes of current interest, such as photocatalysis,[22,23] singlet exciton fission,[24,25] triplet-triplet annihilation,[26] organic photovoltaics,[27,28,29] lasing,[30] fluorescence probing,[31,32,33] and bio-labelling.[34]

As compared to other organic dyes, perylene dyes provide a wealth of opportunities for the tuning of their properties via structural modification. These structural modifications can be achieved at three different positions around the perylene core; namely, the "peri" (3,4,9,10) positions, the "bay" (1,6,7,12) positions, and the "ortho" (2,5,8,11) positions (Figure 1). Among these, the functionalization of peri and bay positions have been the preferred choices so far. At the peri positions, mostly imide, ester, and benzimidazole groups have been substituted (**A1–D1**; Figure 1). The absorption and emission spectra shift bathochromically upon going from **A1** to **D1**.[5,20] These peri-substituents influence other properties as well. Generally, the ester functionalized derivatives are the least electron-deficient and exhibit the best solubility.[9,32] On the other hand, the imide and benzimidazole groups significantly increase the electron deficiency of the perylene core but decrease the solubility.[5,20] In particular, the bisbenzimidazole derivatives have extremely low solubility in common organic solvents.[35]

Once the peri positions are functionalized, the bay positions (1,6,7,12) provide an additional "handle" to control the opto-electronic properties of the dye. Simultaneously, the bay substituents significantly increase the solubility of the dye by twisting the otherwise planer perylene core.[1,36,37] For the bay functionalization, 1,7-disubstitution and 1,6,7,12-tetrasubstitution have been used as the two major approaches, for which 1,7-

[a] Laboratory of Organic Materials & Interfaces, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands. E-mail: R.K.Dubey@tudelft.nl; W.F.Jager@tudelft.nl
[b] Laboratory of Optoelectronic Materials, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands.

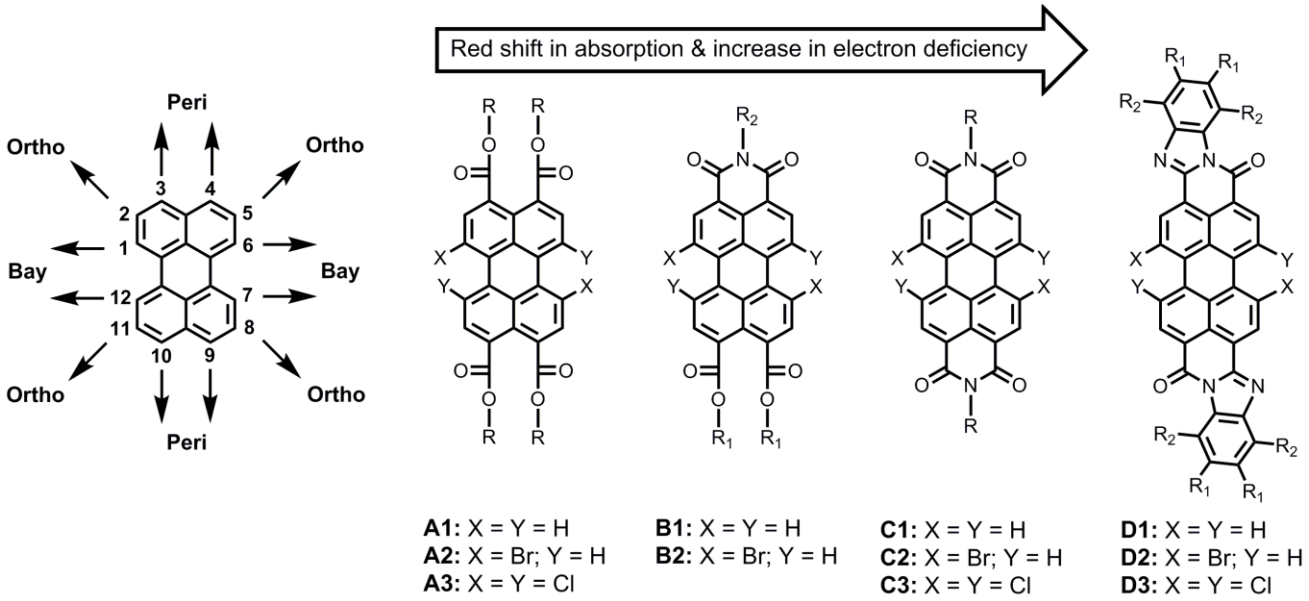


Figure 1. Previously prepared perylene-tetracarboxylic acid derivatives with tunable optical and electronic properties.

dibromo- and 1,6,7,12-tetrachloro-perylene derivatives have been used as precursors, respectively.[3]

Since the halogen atoms can undergo a large variety of substitution and carbon-carbon coupling reactions, the bay-halogenated derivatives (**A2**–**D2** and **A3**–**D3**) are highly valuable and versatile synthons. For attaching substituents to bay area, various methods, such as Suzuki[21] and Sonogashira[38] couplings, and nucleophilic aromatic substitution reactions, mostly with sulfides,[16,39,40] cyclic amines,[14,33,41] and phenols,[5,15,20,41,42] have been reported.

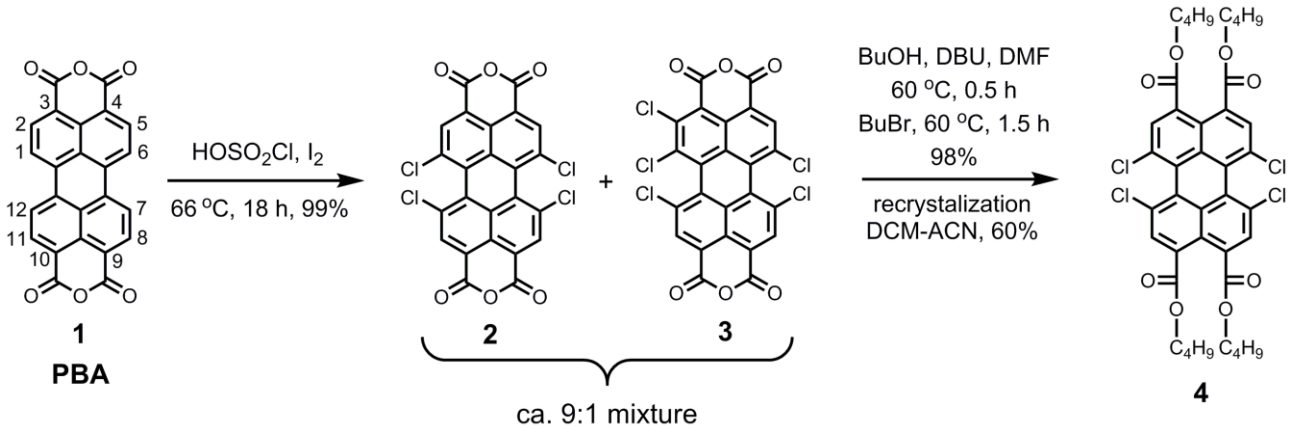
The ortho substitution is an additional and recently developed method to prepare perylene derivatives with altered properties.[43,44,45] Contrary to the bay-substitution, the ortho-substitution does not twist the perylene core. Therefore, this substitution is especially important for applications where planarity of the perylene core is an important requirement. This approach is still in the phase of development and has exclusively been applied on the perylene bisimide derivatives, so far.

We present, herein, the very first synthesis of unsymmetrical peri-substituted 1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxilic acid derivatives **5**–**10**. These bay-chlorinated compounds are excellent starting materials for the synthesis of a large range of perylene derivatives due to the presence of four chlorine atoms that can be easily substituted. In addition, we have modified the conventional synthetic methodology for the tetraphenoxy-bay-substitution to achieve high chemical yield in significantly less reaction time as demonstrated with the synthesis of previously reported tetraphenoxy-bay-area-substituted compounds **12** and **14**.

Results and discussion

Synthesis and Characterization. The synthesis of the pure perylene precursor 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic tetra-*n*-butylester **4** was carried out from commercially available perylene-3,4,9,10-tetracarboxylic bisanhydride (PBA, **1**) and is outlined in **Scheme 1**.

The first step involved the tetra-chlorination of PBA **1** using chlorosulfonic acid. In our recent studies, we showed that the conventional reaction conditions (70 °C, 20 h) to obtain 1,6,7,12-tetrachloro-PBA **2** produces ca. 20% of 1,2,6,7,12-pentachloro-PBA **3** as the side product.[7] In this study, we observed that the amount of the side product 1,2,6,7,12-pentachloro-PBA **3** highly depends on the temperature of the



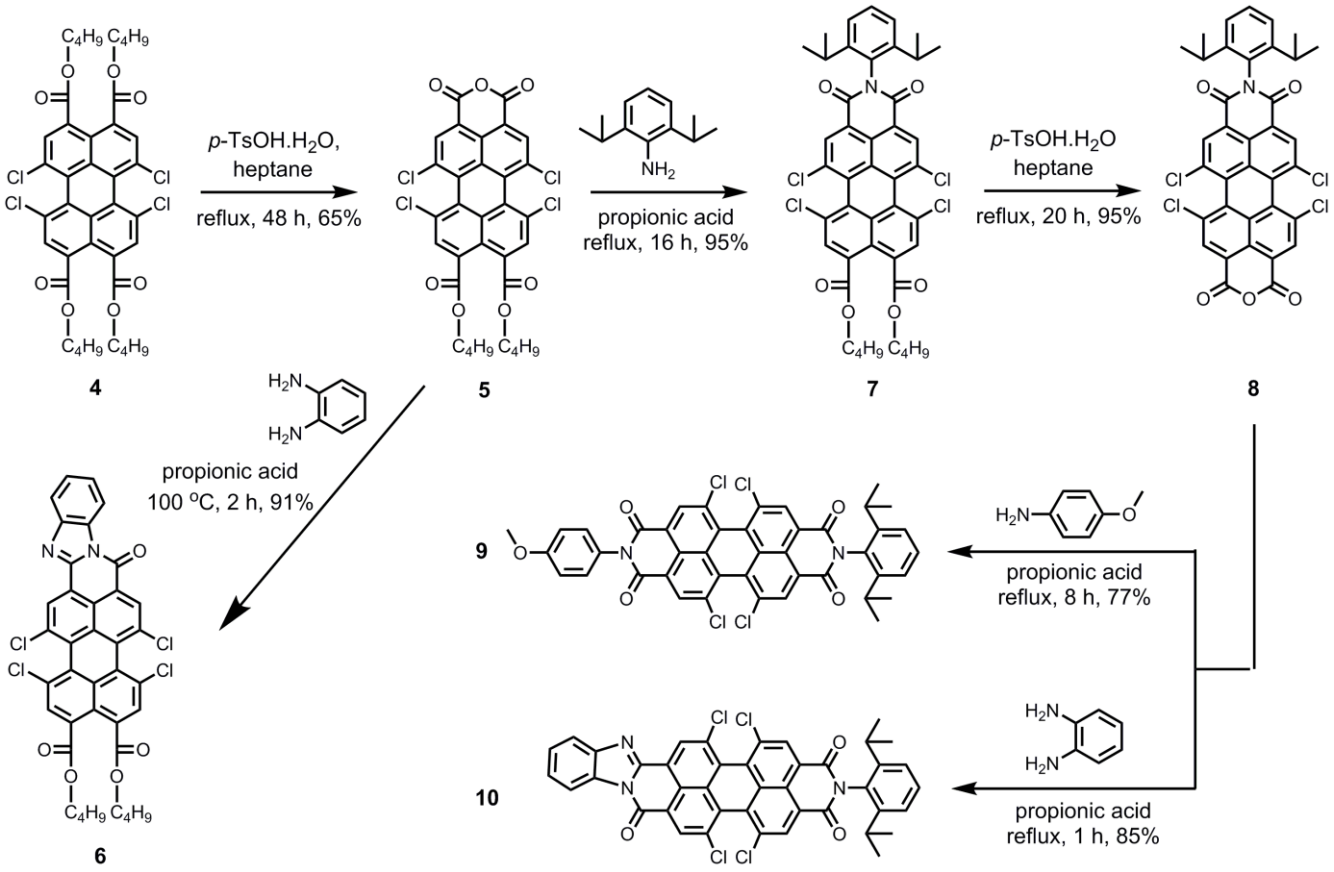
Scheme 1. Synthesis of pure 1,6,7,12-tetrachloroperylene tetra-*n*-butylester 4.

reaction. By keeping the reaction mixture at 66 °C for 16 h, we could reduce the amount of pentachloro impurity to less than 10%. The reaction produced trichloro-derivative at reaction temperatures lower than 66 °C along with the pentachloro-derivative. Hence, a further decrease in the reaction temperature was not possible. In view of the sensitivity of this reaction towards temperature, it is recommended not to use an oil-bath, which often results in large temperature fluctuations. For this reaction, we specifically used aluminum based dry heating block to attain a good temperature control.

In the second step, the crude mixture of **2** and **3** was converted into the corresponding perylene tetra-*n*-butylester derivatives, because these are highly soluble and crystalline compounds. The esterification reaction with *n*-butanol and *n*-bromobutane, in dimethylformamide[46] at 60 °C, was highly efficient and gave a mixture of corresponding tetra- and pentachloroperylene tetra-*n*-butylesters in the expected ratio of ca. 9:1 as revealed by the ^{1}H NMR spectroscopy.[7] Eventually, the desired tetrachloro-derivative **4** was obtained in the pure form by recrystallization from acetonitrile/dichloromethane mixtures in overall 60% yield. It is important to emphasize that the pure compound **4** can also be obtained by silica gel column chromatography, using toluene as the eluent.

Scheme 2 depicts the route to the new peri-substituted perylene derivatives that we have synthesized from pure perylene tetra-*n*-butylester **4**. In the first step, the pure perylene tetra-*n*-butylester **4** was converted to perylene monoanhydride di-*n*-butylester **5** by an acid catalyzed removal of two ester moieties in refluxing *n*-heptane.[5,9] The synthesis of compound **5** was the most challenging step in the whole synthetic scheme because of the simultaneous formation of corresponding tetrachloro-bisanhydride **2**. The yield of the product **5** was found to be highly sensitive to various parameters, such as temperature, amount and type of the solvent, and the amount of *p*-TsOH·H_2O (Table S1, supporting information). Noticeably, the selectivity of this reaction towards yielding **5** was significantly reduced at temperatures higher than 99 °C, in particular when using higher amount of *p*-TsOH·H_2O, and when solvents that are more polar than *n*-heptane were used. This was because of an enhanced formation of the side product perylene bisanhydride **2**. Herein, we maximized the yield of **5** by carrying out the reaction with ca. 1.1 equivalents of *p*-TsOH·H_2O using a limited amount of *n*-heptane at its reflux temperature.

The isolation of compound **5** in pure form was also challenging. Column chromatography could not be employed because the anhydride group of compound **5** strongly adheres to the silica. The further purification attempts based on solubility difference between **5** and **2** also failed. This was mainly because of the moderate solubility of side product **2** in common organic solvents, such as dichloromethane, chloroform, and toluene. The solubility of side product **2** can be explained by the presence of four chlorine atoms at the bay positions. We experienced that alcohols, in particular methanol and ethanol, could not be used for the isolation of compound **5** because alcohols react with compounds **2** and **5** at higher temperatures. Refluxing mixtures of mono anhydride



Scheme 2. Synthesis of novel 1,6,7,12-tetrachloro substituted perylene derivatives 5–10.

5 and bisanhydride **2** in alcohols, resulted in the formation of red and highly fluorescent water-soluble compounds. These compounds are most likely formed by the opening of anhydride functionalities by a nucleophilic attack of an alcohol, thus forming ester carboxylate functionalities on a peri-position. This reaction is known for perylene anhydrides, but only occurs when the strong base DBU is added.[46] The reason why this reaction takes place for tetrachloro perylene anhydrides **2** and **5** without DBU activation, is the higher reactivity of these chlorinated compound. We ascribe this high reactivity to the higher electron deficiency of the perylene core induced by the strongly electron withdrawing bay-chlorines, that is clearly reflected by the lower reduction potential of these compounds. Finally, compound **5** was purified by recrystallization using refluxing acetonitrile in ca. 65% overall yield. The product has the purity of 97% as 3% contamination of bisanhydride still persisted.

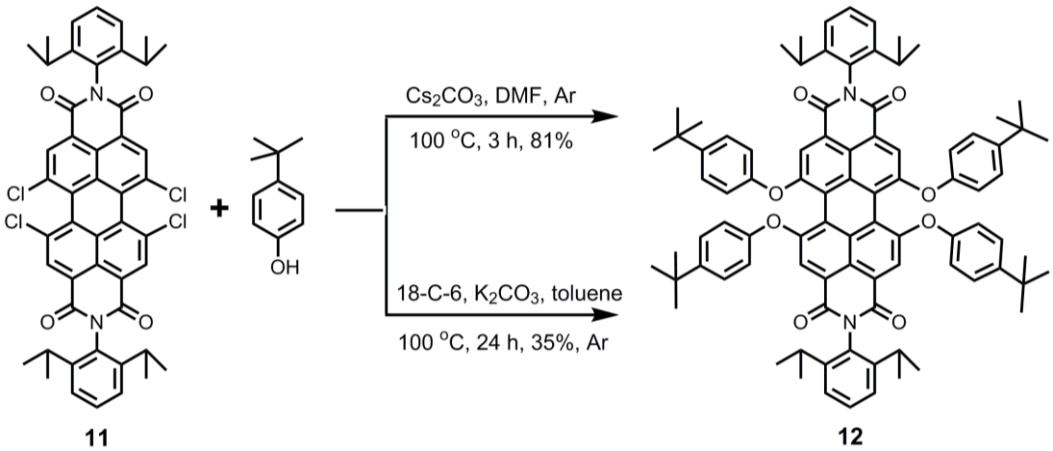
Perylene monoanhydride di-*n*-butylester **5** is an important intermediate because of the presence of free monoanhydride group, which can be utilized to generate new functionalities at the peri-positions. Herein, compound **5** was first reacted with 1,2-diaminobenzene in propionic acid at 100 ^{o}C to get tetrachloroperylene monobenzimidazole di-*n*-butylester **6** in 91% yield.[6] It has to be emphasized that the di-*n*-butylester moieties present on compound **6** can further be converted to monoanhydride group, which can be used as active site to prepare unsymmetrically substituted bisbenzimidazoles.

The imidization of the anhydride **5** with 2,6-diisopropylaniline was performed in refluxing propionic acid to achieve tetrachloroperylene monoimide di-*n*-butylester **7** in an extremely high yield (95%). Clear enough, the ester functionalities in **5**, as well as the chlorine atoms at the bay area, were stable under these harsh reaction conditions. Subsequently, the di-*n*-butylester moieties of compound **7** were converted to monoanhydride functionality by the treatment with an excess of *p*-TsOH·H_2O in refluxing *n*-heptane. This reaction resulted in an hitherto unknown compound 1,6,7,12-tetrachloroperylene monoimide monoanhydride **8** in 95% yield. Compound **8** is an important intermediate, which is capable of providing an easy access to unsymmetrical 1,6,7,12-tetrachloroperylene bisimides and 1,6,7,12-tetrachloroperylene monoimide monobenzimidazoles. To prove this point, compound **8** was converted to unsymmetrical perylene bisimide **9** by the reaction of 4-methoxyaniline in high yield. Furthermore, the synthesis of the unsymmetrical perylene monoimide monobenzimidazole derivative **10** was also carried out in 85% yield by treating **8** with 1,2-diaminobenzene in propionic acid at reflux.

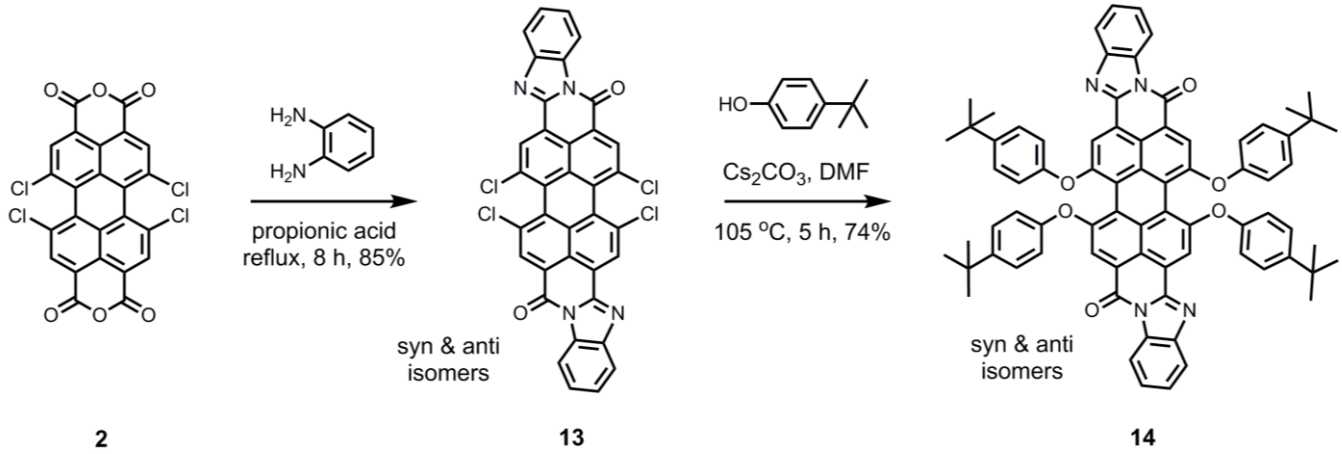
The starting compound 1,6,7,12-tetrachloroperyle tetraester **4** can also be used for the synthesis of pure 1,6,7,12-perylene bisanhydride **2**, which is a highly important intermediate to obtain perylene bisimides (like **11**). This is done by using an excess of *p*-TsOH·H_2O at higher dilution in *n*-heptane and reflux conditions for 24 h (Scheme S1, Supporting Information). Subsequently, the imidization of bisanhydride **2** with 2,6-diisopropylaniline was performed in refluxing propionic acid and corresponding perylene bisimide **11** was obtained in 91% yield.

In view of the issues associated with low solubility of perylene bisimides, the substitution of the four bay-chlorine atoms by the phenoxy groups to give 1,6,7,12-tetraphenoxyperylene bisimides (like **12**) is a highly desirable process (Scheme 3). The presence of four phenoxy groups at the bay-area generally results in dramatic increase in solubility. This nucleophilic aromatic substitution reaction has been extensively performed with various phenols in the presence of K_2CO_3 in NMP. The literature shows that a wide range of reaction times (8–48 h)[47,48] and reaction temperatures (80–140 ^{o}C)[49,47] have been employed to perform this reaction, for which low to extremely high yields (30–95%)[42,49] have been reported.

In this study, we examined the efficacy of two other reactions to produce the tetraphenoxy derivative **12** (Scheme 3). In first method, tetrachloroperylene bisimide **11** was treated with 4-*tert*-butylphenol in the presence of Cs_2CO_3 in DMF at 100 ^{o}C.[5] Interestingly, the reaction was completed in only 3 hours and a high yield (81%) was achieved. Because of the short reaction time, this methodology provides a promising alternative to the exclusively used K_2CO_3/NMP



Scheme 3. Synthesis of 1,6,7,12-tetraphenoxyperylene bisimide 12.



Scheme 4. New direct approach to synthesize 1,6,7,12-tetraphenoxyperylene bisbenzimidazole 14.

reaction, which requires longer reaction times. In the second method, 4-*tert*-butylphenol was reacted with compound **11** in the presence of K_2CO_3 and 18-crown-6 was used as the phase transfer catalyst in toluene at 100 °C. This reaction has been previously employed on 1,7-dibromoperylene bisimides and was found to be quite fast and efficient.[14,41] However, in this case, a maximum yield of only 35% could be obtained for compound **12** even after long reaction time (24 h). Interestingly, the reaction also yielded the triphenoxy-substituted product in a noticeable amount (ca. 30%).

As depicted in Scheme 2, the perylene derivatives with one free monoanhydride group (**5** and **8**) are important intermediates for the synthesis of corresponding derivatives with one benzimidazole group at the peri-position (**6** and **10**). The presence of benzimidazole group results in an extension of π-system of the perylene core.[35] This effect significantly reduces the solubility of the dye. The solubility is still manageable for the monobenzimidazole derivatives (e.g. **6** and **10**) due to the presence of better soluble groups on the other side of perylene core.[8] However, for the bisbenzimidazole perylene derivatives, tetraphenoxy-bay-substituents are essential to achieve moderate solubility in common organic solvents.[10,35] Previously, the synthesis of tetraphenoxy-bay-substituted bisbenzimidazoles was performed in an indirect manner from 1,6,7,12-tetraphenoxyperylene bisanhydrides, which were obtained by the saponification of 1,6,7,12-tetraphenoxyperylene bisimides as described in Scheme S2 (Supporting Information).[10,35]

In this study, we followed a direct route for an efficient synthesis of bisbenzimidazoles with solubilization improving tetraphenoxy groups at the bay area (Scheme 4). First, 1,6,7,12-tetrachloroperylene bisanhydride **2** was converted into the corresponding 1,6,7,12-tetrachloroperylene bisbenzimidazole **13** by treatment with 1,2-diamonobenzene in refluxing propionic acid, resulting in 85% yield. As expected, compound **13** exhibited poor solubility, so that further reaction for phenoxy-substitution in NMP could not be realized. Therefore, similar to perylene bisimides, the coupling reaction of compound **13** with 4-*tert*-butylphenol was performed in DMF and it proceeded smoothly at 105 °C to afford the desired product **14** in 74% yield. In the aromatic region of ^{1}H NMR spectrum of **14**, the presence of syn- and anti-isomers is evident by the appearance of four singlets (between 8.4 to 8.6 ppm) originating from perylene core protons (Figure 2).[10] The integration of these singlets revealed the presence of these isomers in a ratio of ca. 3:2. The unambiguous assignment of these singlets to particular isomers could not be done due the extensive overlapping of NMR signals. Therefore, it cannot be determined which is the prevailing isomer. Noticeably, the two isomers were reported in 1:1 ratio, when the tetraphenoxy-bisbenzimidazoles were prepared from 1,6,7,12-tetraphenoxy-perylene bisanhydrides in quinolone at 220 °C.[10]

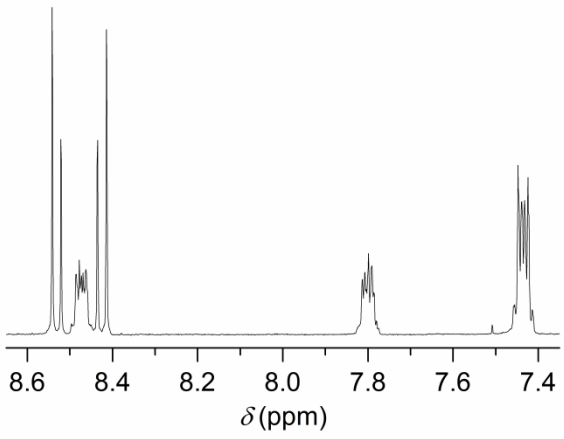


Figure 2. The ^{1}H NMR spectrum (aromatic region) of compound 14.

Electrochemical Properties. The electrochemical characterization has been carried out using cyclic voltammetry (CV) to understand the electron-accepting nature of the synthesized chromophores **4**, **6**, **7**, and **10**–**14**. The obtained redox potentials in dichloromethane versus Fc/Fc^+, together with calculated HOMO and LUMO energy levels versus vacuum, are listed in Table 1.

Table 1. Redox potentials (vs Fc/Fc^+) and electronic energy levels (vs vacuum) of perylene derivatives 4, 6, 7, and 10–14.[a]

Compd	E_{1red}	E_{2red}	E_{1ox}	E_g (eV)[f]	E_{LUMO} (eV)[g]	E_{HOMO} (eV)[h]
4	–1.30	–1.52	–[b]	2.53	–3.50	–6.03
6	–0.95	–1.17[d]	–[b]	2.16	–3.85	–6.01
7	–0.95	–1.31[c]	–[b]	2.35	–3.85	–6.20
10	–0.78	–0.98	–[b]	2.06	–4.02	–6.08
11	–0.78	–1.00	–[b]	2.25	–4.02	–6.27
12	–1.17	–1.39[c]	+0.84	2.00	–3.63	–5.63
13	–[e]	–[e]	–[e]	1.94	–[e]	–[e]
14	–1.15	–1.31	+0.72	1.83	–3.65	–5.48

[a] The redox potentials (V vs Fc/Fc^+) measured by cyclic voltammetry in dichloromethane (Scan rate = 0.10 V/s). The potentials are reported as $E_{1/2}$ (= ($E_p^a + E_p^c$) / 2) and quoted to the nearest 0.01 V. [b] Not observed. [c] Quasi-reversible. [d] Not visible very clearly. [e] Could not be measured because of poor solubility. [f] Optical band gap calculated from equation $E_g = hc/\lambda$a.e. ≈ 1240/λa.e.(nm); Where λa.e. denotes the absorption edge wavelength in nm, obtained from offset wavelength derived from the low energy absorption band.[50] [g] Estimated vs vacuum level from $E_{LUMO} = -(E_{1red} + 4.8eV)$. [h] Estimated from $E_{HOMO} = E_{LUMO} - E_g$.

The perylene derivatives mostly used for applications are the archetypal perylene bisimides (e.g. **11**). In general, the perylene bisimides are good *n*-type semiconductors due to the presence of two electron-withdrawing imide groups, that exhibit two reversible reduction waves at low negative potentials corresponding to the formation of the radical anion and dianion.[1]

In this series of compounds, the perylene tetraester **4** exhibits first reduction potential at ca. –1.30 V, i.e. the most negative value in this series. This means, it is the least electron deficient compound. Upon moving to compounds **6** and **7**, the electron deficiency increases because of the presence of either a benzimidazole or an imide group, respectively, that are more electron-withdrawing than the ester groups. Notably, both compounds **6** and **7** exhibit a first reduction at same potential. It means that the benzimidazole and imide groups exert electron-withdrawing effect of the same magnitude on the perylene core. The compound **10**, with one imide and one benzimidazole groups, and perylene bisimide **11** exhibit the least negative values of first and second reduction potentials. Therefore, they are the most electron-deficient compounds in the series. It is worth noting that four electron-withdrawing bay-chlorine atoms make these derivatives comparatively more electron deficient than the corresponding derivatives with no bay-substituents.[9] In the case of compounds **12** and **14**, the presence of four phenoxy substituents at the bay-area clearly exerts a negative impact on the electron deficiency of the perylene core. For these compounds, the first reduction occurs at significantly more negative potential (ca. –1.15 V) compared to that (ca. –0.78 V) observed for similar perylene derivatives with four chlorine atoms (**10** and **11**).

Absorption and Emission Properties. The normalized absorption and emission spectra of the compounds **4**, **6**, **7**, and **10–14** in chloroform are shown in Figure 3, and the relevant optical data of these compounds are summarized in Table 2.

All the compounds exhibit well-defined S_0–S_1 absorption and emission bands in the visible region, which is a characteristic feature of the aromatic perylene core. However, a systematic trend has been displayed by these compounds in their optical profile depending on the substituents either at "peri" or "bay" positions. The perylene tetraester **4**, which carries four chlorine atoms at bay-positions, has the most blue-shifted absorption (λ_{max} = 457 nm) and emission (λ_{max} = 503 nm) spectra. Surprisingly, compound **4** shows a low fluorescence quantum yield (ϕ_f = 0.26) and life-time (τ_f = 1.6 ns). This is striking because the "bare" perylene tetraester, with no substituents at bay-area, is highly fluorescent with a fluorescence quantum yield of almost unity and a long life-time of 4.0 ns.[51] The perylene monoimide diester **7**, in which two ester groups are replaced by one imide moiety, gives bathochromically shifted absorption (λ_{max} = 496 nm) and emission (λ_{max} = 533 nm) spectra. In addition, an extremely high fluorescence quantum yield (ϕ_f = 0.98) and a long life-time (τ_f = 5.4 ns) is observed for this derivative. A high fluorescence (ϕ_f = 0.91) and a further red-shifted absorption (λ_{max} = 521 nm) and emission (λ_{max} = 550 nm) were observed for perylene bisimide **11**.

For the compounds **6**, **10**, and **13**, which contain either one or two benzimidazole groups at "peri" positions, a larger red-shift of the absorption and emission spectra is observed as compared to that of corresponding derivatives with imide groups (Table 2). This larger red-shift in benzimidazole based derivatives can be explained by an effective extension of π-system of the perylene core.[35] Therefore, attaching a benzimidazole moiety as compared to imide group, works better to achieve bathochromic shifts in absorption and emission spectra. However, the presence of benzimidazole moiety clearly reduces the fluorescence quantum yield as compared to imide groups. Surprisingly, the benzimidazoles **6**, **10**, **13**, and **14** possess long fluorescence life-times, which identifies low rates of fluorescence (k_F) along with higher quenching rates (k_Q), the cause for the low fluorescence quantum yields of these compounds (Table 2).

Along with "peri" substitutions, the "bay" substitution also influences the optical properties of perylene dye. The tetraphenoxy-bay-substituents present in the derivatives **12** and **14** further shift the absorption band to longer wavelengths by 47–64 nm. This significant bathochromic shift was observed in emission spectra as well. These observations verify the importance of both "peri" and "bay"-functionalizations to fine-tune opto-electronic properties of perylene chromophores.

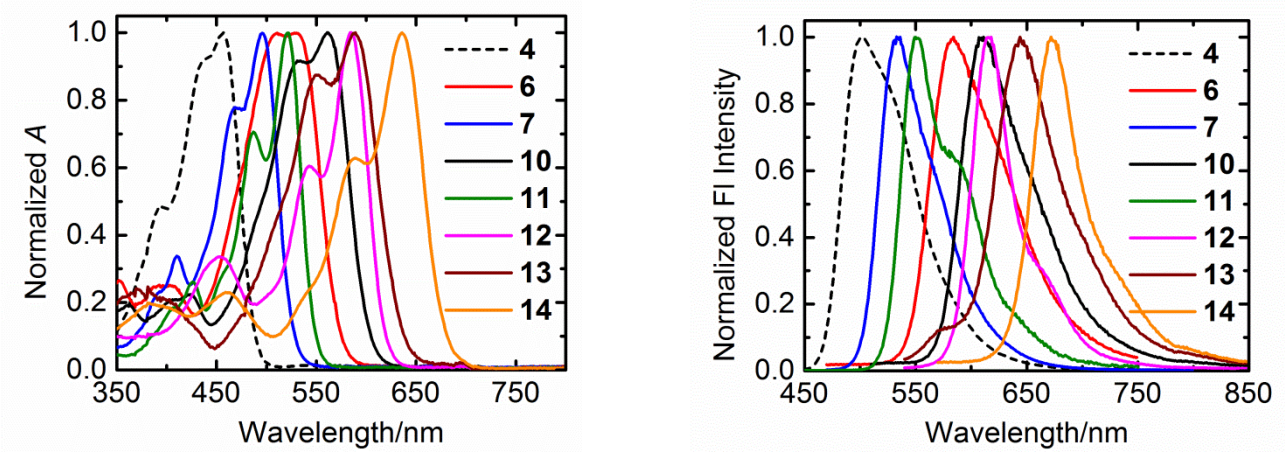


Figure 3. The normalized UV/Vis absorption (Left) and emission (Right) spectra of synthesized compounds in chloroform.

Table 2. Optical properties of the compounds 4, 6, 7, and 10–14 in chloroform.

Compd	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	Stokes shift (cm^{-1})	Φ_f [a]	τ_f (ns) [b]	k_F [c] (10^8 s^{-1})	k_Q [d] (10^8 s^{-1})
4	457	25400	503	2001	0.26	1.6	1.63	4.63
6	530	34200	584	1745	0.36	4.8	0.75	1.33
7	496	38800	533	1400	0.98	5.4	1.81	0.04
10	561	44000	611	1459	0.38	4.7	0.81	1.32
11	521	46900	550	1012	0.91	4.9	1.86	0.18
12	585	53600	618	913	0.72	6.3	1.14	0.44
13	589	–[e]	644	1450	0.28	4.3	0.65	1.67
14	636	50700	672	842	0.20	5.0	0.40	1.60

[a] Fluorescence quantum yield. [b] Fluorescence life-time. [c] Rate of fluorescence. [d] Rate of fluorescence quenching. [e] Could not be measured because of poor solubility.

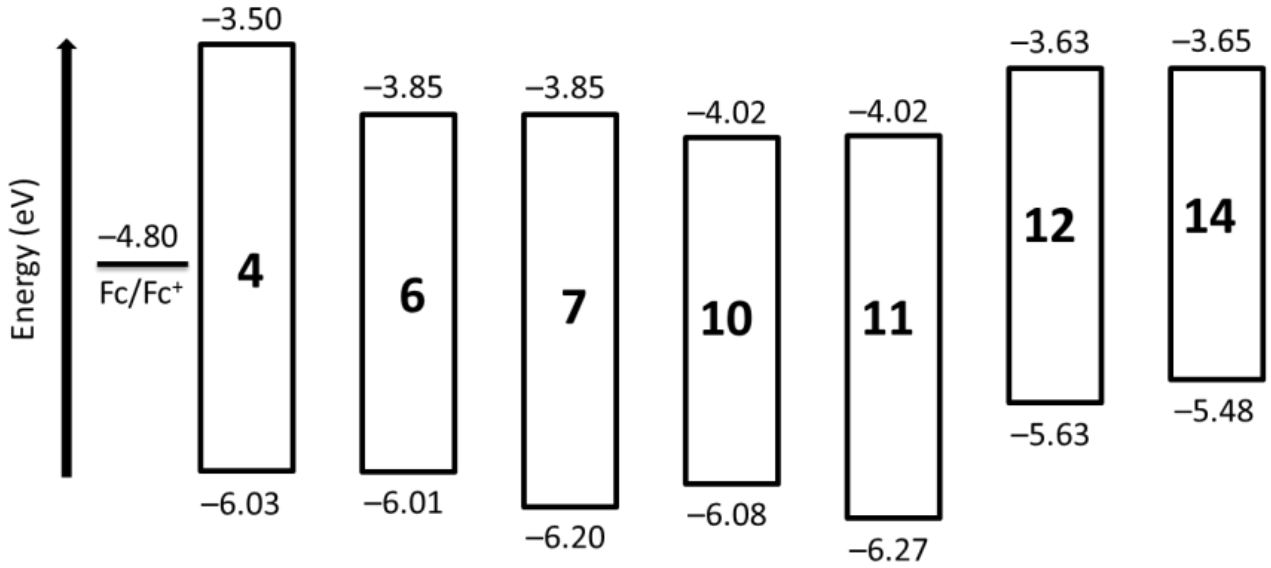


Figure 4. The HOMO and LUMO levels of synthesized perylene derivatives against vacuum.

The HOMO and LUMO levels of synthesized perylene derivatives are shown in Figure 4, which depicts the clear effect of peri and bay substitution on the electronic structure of perylene core. A noticeable feature is that the derivatives with benzimidazole group (e.g. **6**) and the corresponding derivatives with imide group (e.g. **7**) exhibit almost same LUMO energy levels. However, their HOMO levels are significantly different.

Conclusions

We have devised an efficient and convenient synthetic methodology for the preparation of novel unsymmetrically "peri"-substituted perylene-3,4,9,10-tetracarboxylic acid derivatives **5–10** starting from pure tetrachloroperylene tetra-*n*-butylester **4**. The efficient preparation of unsymmetric tetrachloroperylene monoanhydride di-*n*-butylester **5** and the inertness of the bay-chlorine atoms and ester functionalities under the applied reaction conditions are the major factors contributing to the success of our method. The newly synthesized derivatives have four chlorine atoms at the 1,6,7,12-bay-positions of perylene core and therefore they are excellent starting materials for the synthesis of a large variety of perylene derivatives bearing bay-area substituents. We have achieved tetraphenoxy-bay-substitution on 1,6,7,12-tetrachloro-perylene bisimide and perylene bisbenzimidazole compounds with high yields in remarkably shorter reaction time using modified reaction conditions. The synthesized compounds displayed systematic trends in optical and electrochemical properties as a function of structure modification at "peri" positions. In this way, the synthetic modifications described in this manuscript provide excellent control over the opto-electronic characteristics of the obtained materials. The studied derivatives altogether are capable of absorbing light in a broad range of visible region of solar spectrum (i.e. 350–700 nm), which makes them highly desirable compounds as photo-functional materials. Further studies focusing on the selective bay-functionalization of the perylene core to produce promising materials for optoelectronic and photovoltaic applications are currently underway and will be reported in due course.

Experimental Section

Materials. All the reagents utilized in the synthesis were purchased from commercial suppliers and used as received 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 were performed by column chromatography. The TLC plates and the sorbent for the column chromatography (silica gel 40–63, mesh size 0.230–0.400 mm) were purchased from commercial suppliers.

Instrumentation and Characterization. The NMR spectra were recorded with 400 MHz pulsed Fourier transform NMR spectrometer in $CDCl_3$ at room temperature. The ^1H NMR spectra of compounds **2** and **13** were measured in D_2SO_4 and CF_3COOD, respectively. The chemical shifts are quoted relative to $CDCl_3$ [δ = 7.26 ppm (^1H, singlet); 77.00 (13C, triplet)]. The chemical shift values are given in ppm and *J* values in Hz. High-resolution mass spectra were collected on an AccuTOF GCv 4G, JMS-T100GCV, Mass spectrometer (JEOL, Japan). The FD/FI probe (FD/FI) was equipped with an FD Emitter, Carbotec (Germany), FD 10 µm. Typical measurement conditions were as follow: Current rate 51.2 mA/min over 1.2 min; Counter electrode –10 kV; Ion source 37 V. The samples were prepared in dichloromethane.

Electrochemical behavior of the compounds was studied using cyclic voltammetry (CHI 600D electrochemical analyzer) in a three-electrode single-compartment cell consisting of a platinum wire in glass as the working electrode, silver wire as the reference electrode, and a platinum sheet as the counter electrode. The cell was connected to the computer controlled potentiostat (CH Instruments Inc. 600D). Pre-dried CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate was used as solvent. The measurements were done under continuous flow of nitrogen. The concentration of the prepared samples was ca. 0.5 mM. Under these experimental conditions, the ferrocene oxidation was observed at 0.52 V. The potentials of all the reversible peaks are reported as $E_{1/2}$ (= (E_p^a + E_p^c) / 2) in V vs Fc/Fc^+ and quoted to the nearest 0.01 V. The measurements were carried out at 0.10 V/s scan rate.

All the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded with a double beam UV/vis spectrophotometer. The emission spectra were corrected for the wavelength response of the detection system. Fluorescence quantum yields were determined by the comparative method using following compounds as reference: perylene-3,4,9,10-tetracarboxylic tetramethylester (Φ_f = 0.95 in CH_2Cl_2) and *N*,*N*′-bis(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxy bisimide (Φ_f = 0.99 in $CHCl_3$).[51] Fluorescence lifetime measurements were performed on a Lifespec-ps Fluorescence spectrometer from Edinburgh Instruments. Samples were placed in 1 cm quartz cuvettes and degassed prior to the measurement. The time correlated fluorescence was analyzed by exponential tail fit with F900 Lifespec software. The rates of fluorescence (k_F) and rates of fluorescence quenching (k_Q) were obtained from steady state and time-resolved optical measurements using Equations 1a-d.

$$\Phi_{\mathrm{F}} = \frac{k_F}{k_F + k_Q} \qquad (1a)$$

$$\tau_{\mathrm{F}} = \frac{1}{k_F + k_Q} \qquad (1b)$$

$$k_{\mathrm{F}} = \frac{\Phi_F}{\tau_F} \qquad (1c)$$

$$k_{\mathrm{Q}} = \frac{k_F}{\Phi_F} - k_F \qquad (1d)$$

Synthesis of a mixture of 1,6,7,12-tetrachloro- and 1,2,6,7,12-pentachloro-perylene-3,4,9,10-tetracarboxy bisanhydride (2+3) from perylene-3,4,9,10-tetracarboxy bisanhydride (1): A mixture of perylene-3,4,9,10-tetracarboxy bisanhydride **1** (10.00 g, 25.49 mmol) and iodine (1.66 g, 6.56 mmol), in chlorosulfonic acid (60 mL), was stirred for 18 h at 66 ^{o}C on aluminum based dry heating block. The reaction mixture was poured into an ice-water mixture, and the solid was collected by filtration using a glass filter. The solid residue was washed with several portions of water and dried under vacuum to afford the crude product (13.37 g, 99%). It was contaminated with 5–10% of corresponding pentachloro-derivative as evident by the small peak at 8.78 ppm in NMR spectrum.[7] ^{1}H NMR (400 MHz, D_2SO_4): δ = 8.75 ppm (s, 4H). ^{13}C NMR spectrum could not be measured because of its low solubility. MS (FD-TOF): $[M]^+$ Calculated for $C_{24}H_4Cl_4O_6$ (529.8736) and $C_{24}H_3Cl_5O_6$ (563.8345); found, 529.8848 and 563.8390.

Synthesis of 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxy Tetrabutylester (4): In a 500 mL round-bottomed flask, crude 1,6,7,12-tetrachloroperylene bisanhydride (**2**+**3**) (10.0 g, 18.86 mmol) and DMF (125 mL) were taken. To this mixture, subsequently, butanol (13.8 mL, 150.8 mmol), and DBU (11.3 mL, 75.4 mmol) were added. The resultant mixture was stirred at 60 ^{o}C for 30 min. Thereafter, bromobutane (16.3 mL, 150.8 mmol) was taken in DMF (75)mL. The solution was added to the reaction mixture and the combined mixture was stirred for another 90 min. at 60 ^{o}C. The reaction mixture was poured into water and the precipitate was filtered off on a glass filter, washed with water, and dried. The crude product (14.6 g, 98%) was contaminated with ca. 5–10% of corresponding pentachloro derivative, as evident by the ^{1}H NMR and HR mass analysis. The pure 1,6,7,12-tetrachloroperylene tetrabutylester **4** (8.9 g, 60%) was obtained by the repetitive recrystallization from dichloromethane/acetonitrile as reported previously.[7] The pure product **4** can also be obtained by silica-gel column chromatography. For column chromatography separation, a portion of crude product **4** (1.0 g) was subjected to silica-gel and eluted with toluene to obtain desired compound **4** (0.85 g, 85%) in pure form. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 4H), 4.44–4.32 (m, 8H), 1.87–1.75 (m, 8H), 1.55−1.45 (m, 8H), 1.05−0.96 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 133.9, 133.5, 131.9, 130.7, 127.2, 123.1, 66.0, 30.6, 19.2, 13.8 ppm. MS (FD-TOF): $[M]^+$ Calculated for $C_{40}H_{40}Cl_4O_8$, 790.1455; found, 790.1431.

Synthesis of 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxy Monoanhydride Dibutylester (5): Compound **4** (1.00 g 1.27 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (0.26 g, 1.38 mmol) were taken in *n*-heptane (8 mL). The resulting suspension was stirred at reflux for 48 h. The product **5** starts to precipitate from the reaction mixture after a few hours. After 48 h, the reaction mixture was cooled to room temperature and heptane was evaporated under vacuum. The crude product was washed with a few portions of water and then with methanol to remove impurities based on *p*-toluenesulfonic acid. Subsequently, the dried orange precipitate was refluxed in hexane (100 mL) for ca. 2 h to remove the soluble starting compound **4**. The crude product **5** (0.73 g, 87%) was collected by filtration, which was contaminated with ca. 10% of side product *i.e.* tetrachloroperylene bisanhydride **2**. Finally, the crude product was purified by recrystallization in acetonitrile. In a typical procedure, the crude product (0.73 g) was stirred in refluxing acetonitrile (115 mL) for 2 h. The resultant solution was left at room temperature overnight. The crystals of the product were collected by filteration and dried to obtain the desired product **5** (545 mg, 65%). The product has the purity of ca. 97% as 3% contamination of bisanhydride still persisted. The recrystallization process can be repeated to achieve higher purity. Soxhlet extraction with hexane can also be used as an alternate purification procedure. But it is not a preferred choice because of the sluggishness of this procedure. Purification by column chromatography is not possible as the product sticks to silica. mp = 213 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 2H), 8.13 (s, 2H), 4.41–4.31 (m, 4H), 1.85–1.75 (m, 4H), 1.54−1.45 (m, 4H), 0.99 ppm (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 158.6, 135.1, 134.7, 134.6, 133.9, 132.2, 132.1, 131.5, 130.9, 125.9, 125.1, 123.4, 118.5, 66.3, 30.5, 19.2, 13.7 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{32}H_{22}Cl_4O_7$, 658.0119; found, 658.0105.

Synthesis of 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxy Monobenzimidazole Dibutylester (6): 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy monoanhydride dibutylester **5** (50 mg, 0.08 mmol) and 1,2-diaminobenzene (16 mg, 0.15 mmol) were taken in propionic acid (2 ml). The mixture was stirred at 100 ^{o}C for 2 h. After cooling down to room temperature, the reaction mixture was poured into water. The resultant precipitate was collected by filtration and washed with several portions of water to remove all the propionic acid. The precipitate was dried and chromatographed on silica, eluting with DCM, to afford the pure product (50 mg, 91%). mp = 172 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 8.61 (s, 1H), 8.32–8.27 (m, 1H), 8.14 (s, 1H), 8.13 (s, 1H), 7.71–7.66 (m, 1H), 7.34–7.27 (m, 2H), 4.44–4.32 (m, 4H), 1.88–1.76 (m, 4H), 1.57−1.46 (m, 4H), 1.01 ppm (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 158.6, 147.2, 143.8, 135.2, 134.6, 134.3, 133.9, 133.2, 132.9, 132.2, 131.9, 131.7, 131.1, 130.3, 128.4, 127.1, 126.8, 126.5, 126.4, 126.3, 123.3, 123.1, 122.3, 121.1, 120.5, 115.8, 66.1, 30.6, 19.2, 13.8 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{38}H_{26}Cl_4N_2O_5$, 730.0596; found, 730.0612.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (7): A 50 mL round-bottomed flask was charged with tetrachloroperylene monoanhydride dibutylester **5** (0.95 g, 1.44 mmol), 2,6-diisopropylaniline (0.38 g, 2.14 mmol), and propionic acid (20 mL). The reaction mixture was refluxed for 16 h and then allowed to cool down to room temperature. The reaction mixture was poured into the water to precipitate the crude product. The precipitate was filtered off and washed with several portions of water to remove propionic acid and aniline. The precipitate was dried and chromatographed on

silica, eluting with 2:1 CH_2Cl_2-hexane, to afford the desired product **7** (1.12 g, 95%). mp = 220 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 2H), 8.15 (s, 2H), 7.51 (t, J = 7.9 Hz, 1H), 7.36 (d, J = 7.9 Hz, 2H), 4.45–4.32 (m, 4H), 2.79–2.68 (m, 2H), 1.89–1.79 (m, 4H), 1.59−1.46 (m, 4H), 1.22–1.14 (m, 12H), 1.02 ppm (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 162.5, 145.6, 134.7, 134.5, 133.8, 133.2, 132.1, 131.7, 131.6, 130.0, 129.9, 129.6, 126.5, 124.2, 123.6, 123.4, 122.4, 66.2, 30.5, 29.2, 24.0, 19.2, 13.8 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{44}H_{39}Cl_4NO_6$, 817.1532; found, 817.1518.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (8): Compound **7** (700 mg, 0.85 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (894 mg, 4.70 mmol) were taken in heptane (15 mL). The resulting mixture was refluxed for 20 h and then allowed to cool to room temperature. Thereafter, the reaction mixture was filtered and the solid residue was thoroughly washed with water and a small amount of cold methanol. The residue was dried to obtain the desired product **8** (560 mg, 95%). mp > 350 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 2H), 8.75 (s, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 2.79–2.65 (m, 2H), 1.19 ppm (t, J = 5.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 158.1, 145.2, 135.9, 135.2, 134.5, 133.2, 131.7, 131.3, 129.8, 129.7, 129.4, 128.0, 125.1, 123.9, 123.5, 123.3, 29.0, 23.7 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{36}H_{21}Cl_4NO_5$, 689.0144; found, 689.0142.

Synthesis of *N*-(2,6-Diisopropylphenyl)-*N'*-(4-Methoxyphenyl)-1,67,12-tetrachloroperylene-3,4,9,10-tetracarboxy Bisimide (9): Synthesized from compound **8** (100 mg, 0.15 mmol), 4-methoxyaniline (36 mg, 0.29 mmol), and propionic acid (2 mL). The reaction mixture was refluxed for 8 h. After cooling down to room temperature, the reaction mixture was poured into the water to precipitate the crude product. The precipitate was filtered off and washed with several portions of water to remove all the propionic acid. The precipitate was dried and chromatographed on silica, eluting with CH_2Cl_2, to afford the desired product **9** (89 mg, 77%). mp > 350 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 2H), 8.74 (s, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.78–2.66 (m, 2H), 1.23–1.15 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 162.3, 159.9, 145.6, 135.6, 135.5, 133.4, 133.3, 131.7, 133.6, 130.0, 129.9, 129.4, 128.9, 128.8, 126.9, 124.2, 123.9, 123.7, 123.5, 123.2, 114.9, 55.5, 29.3, 24.0 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{43}H_{28}Cl_4N_2O_5$, 792.0752; found, 792.0726.

Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy Monoimide Monobenzimidazole (10): A mixture of compound **8** (200 mg, 0.29 mmol) and 1,2-diaminobenzene (62 mg, 0.58 mmol) was refluxed in for 1 h in propionic acid (5 ml). After cooling down to room temperature, it was poured into water to precipitate the crude product. The precipitate was filtered off and washed with several portions of water to remove all the propionic acid. The precipitate was dried and chromatographed (silica/DCM) to afford the pure product (187 mg, 85%). mp > 350 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 8.86 (s, 1H), 8.75 (s, 2H), 8.55–8.51 (m, 1H), 7.93–7.90 (m, 1H), 7.55–7.50 (m, 3H), 7.36 (d, J = 7.6 Hz, 2H), 2.78–2.68 (m, 2H), 1.20–1.16 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 158.4, 147.1, 145.6, 143.9, 136.1, 135.5, 135.4, 135.0, 133.5, 133.3, 133.1, 132.2, 131.8, 131.1, 130.0, 129.9, 129.6, 129.3, 128.9, 128.6, 126.8, 126.5, 126.5, 124.2, 124.0, 123.9, 123.3, 122.7, 122.6, 122.1, 120.7, 115.9, 29.3, 24.0 ppm. MS (ESI-TOF): $[M]^+$ Calculated for $C_{42}H_{25}Cl_4N_3O_3$, 759.0650; found, 759.0652.

Synthesis of 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic Bisanhydride (2): Pure compound **4** (2.0 g, 2.53 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (4.8 g, 25.5 mmol) were placed in a round-bottomed flask equipped with a reflux condenser. Subsequently, heptane (35 mL) was added and the reaction mixture was stirred at reflux (ca. 24 h) until the heptane solution became completely clear. The completion of reaction was confirmed by the TLC analysis. Afterwards, the reaction mixture was allowed to cool down to room temperature. The solid residue was collected by filteration, washed with methanol and water several times, and dried to obtain the desired product (1.3 g, 97%). ^1H NMR (400 MHz, D_2SO_4): δ = 8.73 (s, 4H) ppm . ^{13}C NMR spectrum could not be measured because of its low solubility. MS (FD-TOF): $[M]^+$ Calculated for $C_{24}H_4Cl_4O_6$, 529.8736; found, 529.8771.

Synthesis of *N,N'*-Bis(2,6-Diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy Bisimide (11): Prepared from compound **2** according to the previously described procedure.[7] ^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 4H), 7.53 (t, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 4H), 2.83–2.69 (m, 4H), 1.27–1.15 ppm (m, 24H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.3, 145.6, 135.6, 133.4, 131.8, 130.0, 129.9, 128.9, 124.3, 123.9, 123.3, 29.3, 24.0 ppm. MS (FD-TOF): $[M]^+$ Calculated for $C_{48}H_{38}Cl_4N_2O_4$, 848.1566; found, 848.1593.

Synthesis of *N,N'*-Bis(2,6-Diisopropylphenyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy Bisimide (12):[52] The compound was synthesized by the following three methods:

(i) In a 25 mL round-bottomed flask, weighed amounts of 1,6,7,12-tetrachloroperylene bisimide **11** (100 mg, 0.12 mmol), 4-*tert*-butylphenol (124 mg, 0.83 mmol), and Cs_2CO_3 (308 mg, 0.95 mmol) were taken. Subsequently, anhydrous DMF (6 mL) was added and the reaction mixture was stirred at 100 ^oC for 3 h under argon atmosphere. Afterwards, the reaction mixture was poured in water and the precipitate was collected by filteration. The solid residue was washed with water and ethanol. The dried crude product was chromatographed (silica/DCM) to afford the desired product **12** (125 mg, 81%). mp > 350 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.4 Hz, 8H), 6.87 (d, J = 8.4 Hz, 8H), 2.75–2.66 (m, 4H), 1.27 (s, 36H), 1.12 ppm (d, J = 6.4 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 155.9, 152.8, 147.3, 145.6, 133.2,

130.7, 129.4, 126.6, 123.8, 122.7, 120.7, 120.2, 120.1, 119.2, 34.3, 31.4, 29.1, 24.0 ppm.

(ii) 1,6,7,12-tetrachloroperylene bisimide **11** (100 mg, 0.12 mmol), 4-*tert*-butylphenol (124 mg, 0.83 mmol), and K_2CO_3 (114 mg, 0.83 mmol) were stirred in NMP (5 mL) at 100 ^{o}C for 24 h under argon atmosphere. The work-up and purification was carried out according to above mentioned procedure to afford the desired product **12** (112 mg, 73%).

(iii) A mixture of 4-*tert*-butylphenol (248 mg, 1.65 mmol), K_2CO_3 (326 mg, 2.36 mmol) and 18-Crown-6 (624 mg, 2.36 mmol), in dry toluene (30 mL), was stirred for 30 min. at room temperature under argon atmosphere. Subsequently, 1,6,7,12-tetrachloroperylene bisimide **11** (200 mg, 0.24 mmol) was added. The reaction mixture was stirred for 24 h at 100 ^{o}C and allowed to cool to room temperature. The solvent was removed by rotary evaporation and the residue was washed with water and dried. The crude product was subjected to silica gel column chromatography (DCM-hexane, 1:1) to afford the product **12** (108 mg, 35%).

Synthesis of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy Bisbenzimidazole (13): 1,6,7,12-tetrachloroperylene bisanhydride **2** (300 mg, 0.57 mmol), 1,2-diaminobenzene (184 mg, 1.70 mmol), and propionic acid (10 ml) were subjected to a 25 mL round-bottomed flask. The reaction mixture was refluxed for 8 h and, subsequently, allowed to cool to room temperature. It was poured into water and the resultant precipitate was collected by filteration. The precipitate was washed with several portions of water and methanol and dried to afford the product (321 mg, 85%) as a mixture of syn and anti regioisomers. mp > 350 ^{o}C. ^{1}H NMR (400 MHz, CF_3COOD): δ = 9.28 (s, 4H), 9.00 (d, J = 7.6 Hz, 2H), 8.14 (d, J = 7.6 Hz, 2H), 8.03 ppm (m, 4H). ^{13}C NMR spectrum could not be measured because of its limited solubility.

Synthesis of 1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy Bisbenzimidazole (14): In a 25 mL round-bottomed flask, weighed amounts of 1,6,7,12-tetrachloroperylene bisbenzimidazole **13** (60 mg, 0.09 mmol), 4-*tert*-butylphenol (110 mg, 0.73 mmol), and Cs_2CO_3 (232 mg, 0.71 mmol) were taken. Subsequently, anhydrous DMF (10 mL) was added and the reaction mixture was stirred at 105 ^{o}C for 5 h under argon atmosphere. Afterwards, the reaction mixture was poured in water and the precipitate was collected by filteration. The solid residue was washed with water and ethanol. The dried crude product was chromatographed (silica/$CHCl_3$) to afford the desired product **14** (74 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1.2H), 8.52 (s, 0.8H), 8.50–8.46 (m, 2H), 8.44 (s, 0.8H), 8.41 (s, 1.2H), 7.83–7.78 (m, 2H), 7.46–7.40 (m, 4H), 7.30–7.22 (m, 8H), 6.94–6.80 (m, 8H), 1.31 ppm (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.95, 156.15, 156.03, 155.85, 155.77, 153.23, 153.19, 152.83, 148.61, 148.56, 147.44, 147.34, 147.07, 146.97, 143.84, 132.95, 132.91, 131.85, 126.73, 126.69, 125.92, 125.77, 125.71, 123.13, 122.52, 121.84, 121.44, 121.24, 120.60, 120.09, 119.99, 119.96, 119.45, 119.40, 119.21, 119.16, 119.12, 118.87, 118.70, 116.44, 116.26, 115.77, 34.37, 31.47 ppm.

Supporting Information

Cyclic voltammograms of the all the compounds (Figures S1 and S2); ^{1}H and ^{13}C NMR spectra of all synthesized compounds (Figures S4–S15); Mass spectra of all the new compounds (Figures S16–S21).

Acknowledgments

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