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# Perylene Bisimide Dyes with up to Five Independently Introduced Substituents: Controlling the Functionalization Pattern and Photophysical Properties Using Regiospecific Bay Substitution

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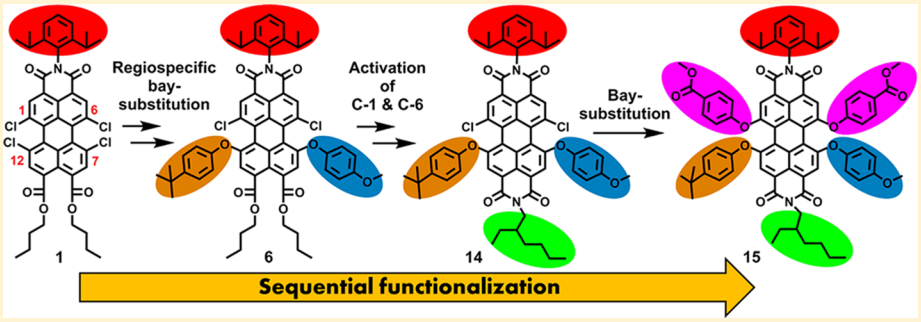
Supporting Information




**ABSTRACT:** We report herein a versatile and user-friendly synthetic methodology based on sequential functionalization that enables the synthesis of previously unknown perylene bisimide (PBI) dyes with up to five different substituents attached to the perylene core (e.g., compound **15**). The key to the success of our strategy is a highly efficient regiospecific 7-mono- and 7,12-diphenoxy bay substitution at the "imide-activated" 7- and 12-bay positions of 1,6,7,12-tetrachloroperylene monoimide diester **1**. The facile subsequent conversion of the diester groups into an imide group resulted in novel PBIs (e.g., compound **14**) with two phenoxy substituents specifically at the 7- and 12-bay positions. This conversion led to the activation of C-1 and C-6 bay positions, and thereafter, the remaining two chlorine atoms were substituted to obtain tetraphenoxy-PBI (compound **15**) that has two different imide and three different bay substituents. The methodology provides excellent control over the functionalization pattern, which enables the synthesis of various regioisomeric pairs bearing the same bay substituents. Another important feature of this strategy is the high sensitivity of HOMO−LUMO energies and photoinduced charge transfer toward sequential functionalization. As a result, systematic fluorescence on−off switching has been demonstrated upon subsequent substitution with the electron-donating 4-methoxyphenoxy substituent.

## INTRODUCTION

Photofunctional materials have received increasing attention over the past two decades owing to their (potential) applications in renewable energy and optoelectronics. Among them, perylene bisimides (PBIs, Figure 1) are highly attractive compounds that exhibit tunable and strong absorption in the visible region together with high photochemical stability and charge carrier mobilities.[1,2] These properties have been utilized in a range of molecular architectures, such as self-assembled supramolecular structures,[3] dendrimers for biolabeling,[4] fluorescent probes,[5−7] light-harvesting arrays,[8−11] and electron donor−acceptor systems.[12−15] PBIs have also found applications in other areas of current interests, such as photocatalysis,[16,17] solar water splitting,[18] singlet exciton fission,[19,20] triplet−triplet annihilation,[21] gas sensing,[22] and organic electronics[23] and photovoltaics.[24]

One of the important features of PBIs is the wealth of opportunities for the attachment of substituents at three different positions around the perylene core: namely, the "imide", the "bay" (1,6,7,12), and the "ortho" (2,5,8,11) positions (Figure 1). Functionalization of the imide and bay positions has been the convenient choice so far because of the availability of easy, versatile, and straightforward synthetic protocols.[25] The imide substituents exert a direct effect on the self-assembly of the dye, and the bay substitutions tune the optoelectronic properties. For the bay functionalization, 1,7-di- and 1,6,7,12-tetrasubstitutions have been used as the major approaches for which 1,7-dibromo- and 1,6,7,12-tetrachloroperylene bisanhydrides (PBAs) have been used as precursors, respectively.[2] In the conventional synthetic protocol, the first step is always the imidization of PBAs with either aliphatic or aromatic primary amines to give PBIs with identical imide substituents (symmetric PBI-$Cl_4$, Figure 2). Afterward, all the

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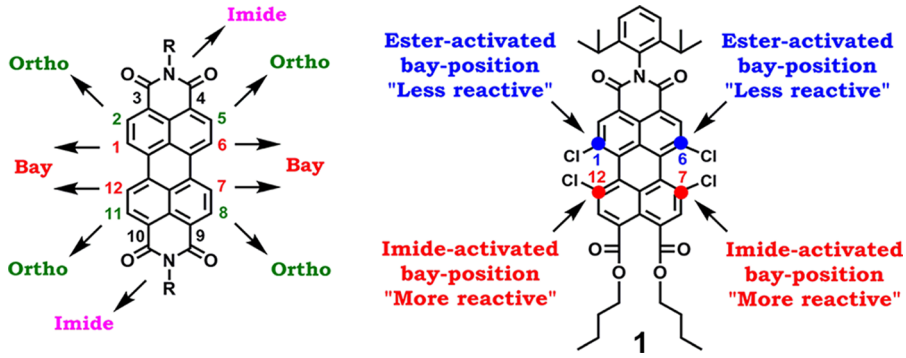


**Figure 1.** (Left) Chemical structure of perylene bisimide and (right) 1,6,7,12-tetrachloroperylene monoimide diester used in this work as the starting compound.

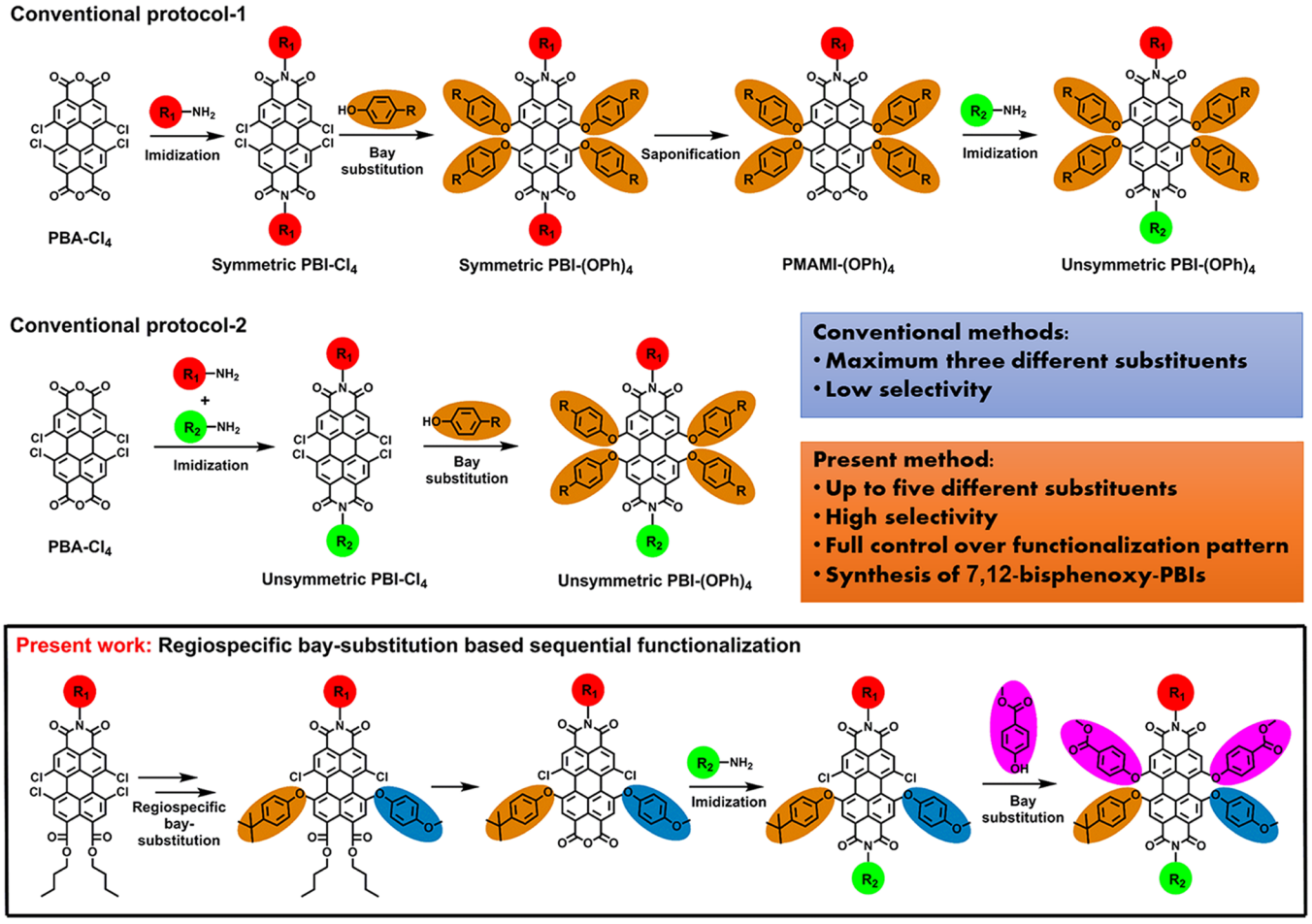


**Figure 2.** Overview of the conventional protocols and present methodology for the synthesis of tetra-bay-substituted perylene bisimides.

bay halogens (four chlorine or two bromine atoms) are substituted simultaneously to facilitate the formation of PBIs bearing the identical bay substituents [symmetric PBI-$(OPh)_4$, Figure 2].[1,26,27]

For "symmetric" 1,7-dibromo-PBIs, bay substitution with identical substituents is performed routinely. Subsequent bay substitution with different substituents employing $S_NAr$ reactions has been reported on a few special occasions only.[28,13,29] Similarly, since the first synthesis of tetrachloro-PTCAs in 1988,[30,31] bay substitution with four identical substituents on tetrachloro-PBIs has been reported almost exclusively. There are only a few exceptions in the literature where substitution of one,[7,32,33] two,[33,34] or three[33] chlorines has been executed. Substitution of two chlorines has been achieved by Würthner et al.[34] and Fernández Lázaro et al.[33] by the regioselective 1,12-substitution using bifunctional reactants, biphenol and ethane-1,2-dithiol, respectively. The most successful attempt to attach different substituents at the bay positions so far has been reported by Fernández Lázaro et al.[33] By employing a fluoride-assisted substitution with aliphatic alcohols and thiols, subsequent substitution of chlorines on "symmetric" tetrachloro-PBIs was achieved, albeit without controlling the regioselectivity of the substitution process.


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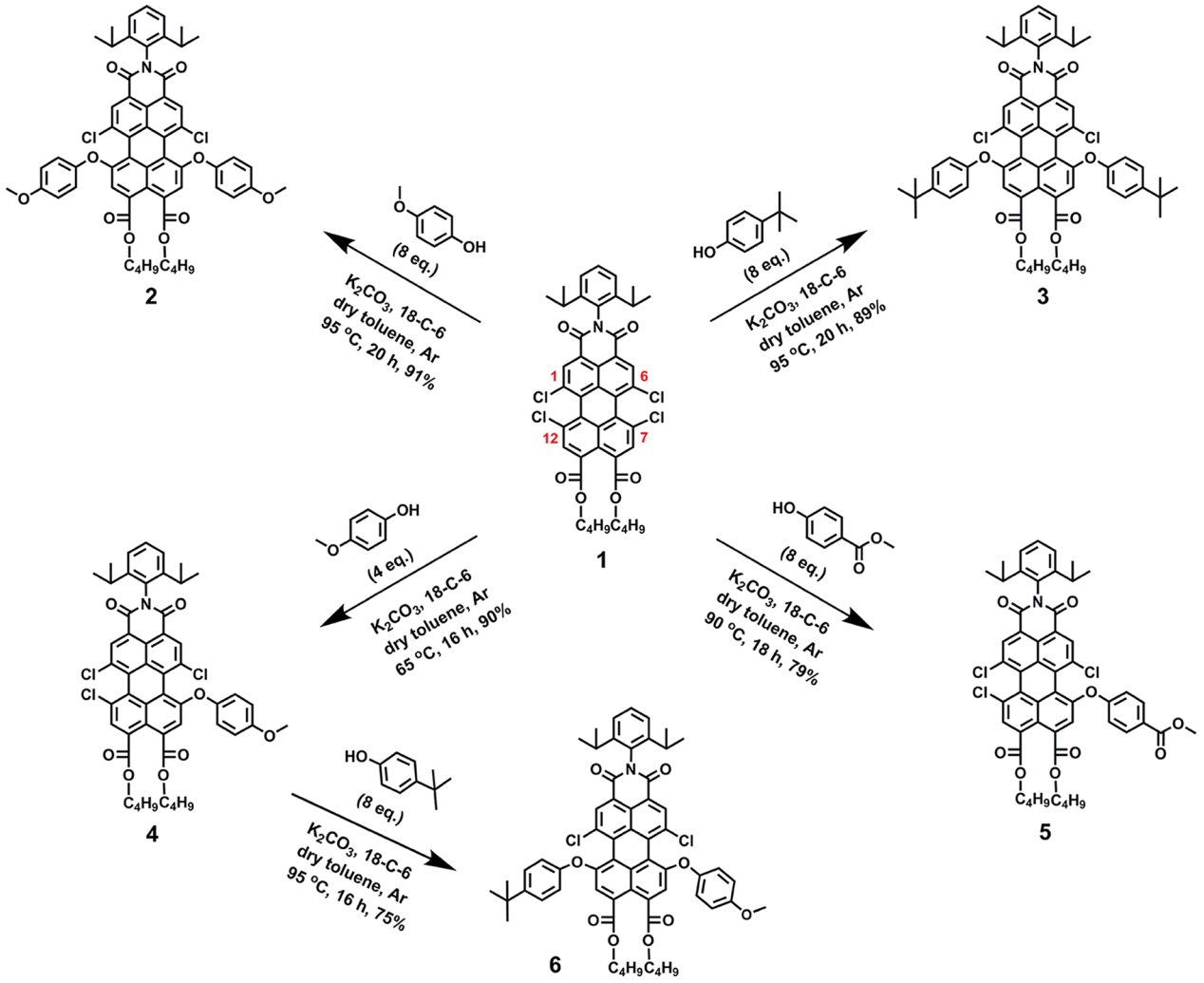
**Scheme 1. Regiospecific 7-Mono- and 7,12-Diphenoxy Substitution on 1,6,7,12-Tetrachloroperylene Monoimide Diester 1**




Notably, this method yielded mono- and trisubstituted products and regioisomeric mixtures of disubstituted products.

Having two different imide substituents is of practical importance, and these PBIs (so-called unsymmetric PBIs) have been synthesized either by converting one of the PBI imide groups into anhydride using saponification[35,36] or by one-step reactions in which two different amines react simultaneously with 1,6,7,12-tetrachloro-PBA (protocols 1 and 2, Figure 2).[37,38] Notably, the non-selective nature of these reactions leads to low yields and a mixture of different products, which are often difficult to separate. However, these procedures have been routinely used as they yield PBIs with up to three different substituents, i.e., two at the imide and one at the bay positions (unsymmetric PBI-$(OPh)_4$, Figure 2).[4,39]

Precise control over the substitution pattern is of utmost importance when it comes to more demanding and specific applications as well as for the realization of complex covalent and supramolecular structures. Since the conventional synthetic procedures do not allow good control over functionalization, the potential of PBIs has not been explored to their full extent. Researchers often have to compromise with the desirable design and properties because of the constraints emerging from the synthesis. In the case of perylene dyes, exact positioning of all substituents is essential considering the fact that their optoelectronic properties and morphology are strongly influenced by the position of the substituents. These pronounced positional effects are evident in photoinduced charge transfer,[28,40,41] intersystem crossing,[42] molecular probes,[6] and also molecular packing in the solid phase.[43−45] Consequently, better control over the substitution pattern around the perylene core is highly relevant.

Recently, we reported the synthesis of a series of 1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic acid derivatives.[46,47] Among them, 1,6,7,12-tetrachloro-perylene monoimide diester **1** (Figure 1) is a unique derivative as it has a stronger electron-withdrawing imide group at one side of the "peri"-region compared to two ester groups at the other side. This induces a distinct reactivity difference between the highly reactive "imide-activated" 7/12 and the less reactive "ester-activated" 1/6 bay positions.[48]

In this work, we have utilized this pronounced difference in reactivity of the bay halogens of 1,6,7,12-tetrachloro-perylene monoimide diester **1** to achieve sequential functionalizations at both imide and bay positions. This eventually led to the PBI dyes with up to five independently introduced substituents, which were not accessible with the conventional protocols. Along with the pronounced deactivation toward $S_NAr$ reactions after each bay substitution, this reactivity pattern allows for the subsequent substitution of all four bay chlorine atoms. Notably, the regiospecific formation of 7,12-disubstituted



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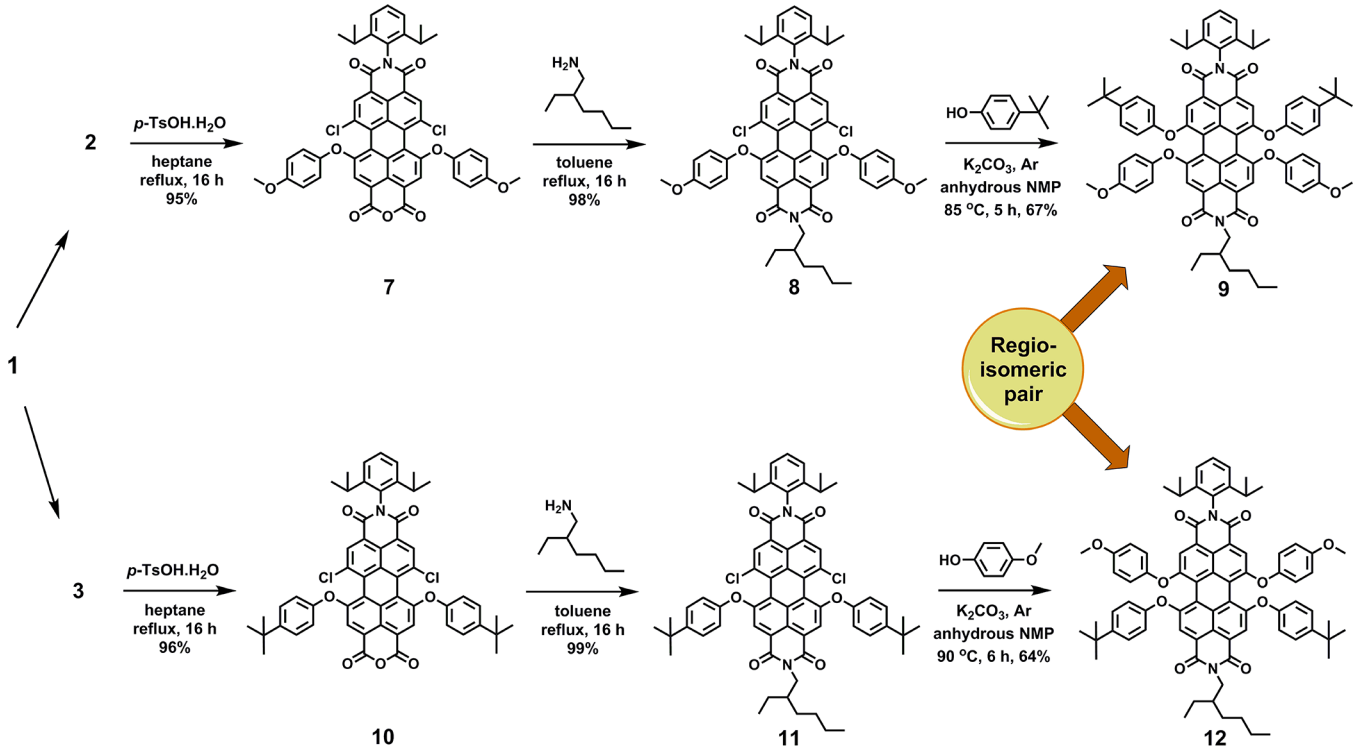
**Scheme 2. Synthesis of Novel 1,6,7,12-Tetraphenoxy-PBI Regioisomers (9 and 12) with Four Different Substituents by Reversing the Order of Bay Substitution**




compounds bearing non-identical substituents is unprecedented. In order to accomplish the remaining two bay substitutions, the ester functionalities were transformed into a second activating imide group in the reaction sequence. In the thus-obtained unsymmetric PBIs, the remaining chlorine atoms at bay positions 1 and 6 are reactive enough to achieve, finally, substitution of all bay positions. Aromatic 2,6-diisopropylphenyl and aliphatic 2-ethylhexyl groups have been chosen as the two different imide substituents. For the bay positions, three different phenoxy groups (i.e., 4-methoxyphenoxy, 4-*tert*-butylphenoxy, and 4-methoxycarbonylphenoxy) were chosen because of their different nucleophilicities and distinct signals in the NMR spectra. This was essential for the identification of the substitution pattern by NMR spectroscopy. The substitution pattern was unambiguously confirmed using various 1D and 2D NMR techniques, most importantly $^{1}H-^{1}H$ COSY and NOESY, and $^{1}H-^{13}C$ HMBC.

## RESULTS

**Synthesis and Characterization.** The recently reported perylene derivative 1,6,7,12-tetrachloro-perylene monoimide diester **1** has been used as the starting compound for our synthesis, as outlined in Scheme 1.[46] The first step, which was also the most crucial step, involved the regiospecific 7-mono- and 7,12-diphenoxy substitution at the perylene core. Previously, nucleophilic aromatic substitution reactions have been extensively performed on 1,6,7,12-tetrachloro-PBIs with various phenols in the presence of $K_2CO_3$ in anhydrous NMP. The literature shows that a wide range of reaction times (8−48 h)[49,50] and reaction temperatures (80−140 °C)[49,51] has been used. These reaction conditions resulted in an exclusive substitution of all the four bay chlorines to give 1,6,7,12-tetraphenoxy-PBIs, usually, in high yields. We first employed this procedure to carry out phenoxy substitution on compound **1**. However, the ester moieties hydrolyzed under these polar and basic reaction conditions even at low temperatures. This was unexpected based on the fact that the ester moieties of corresponding 1,7-dibromo-perylene derivatives were found to be robust even under harsher reaction conditions.[6]

We subsequently moved to non-polar toluene as the solvent in the presence of a $K_2CO_3$−18-crown-6 mixture, a reaction that has been routinely used for the phenoxy substitution on 1,7-dibromo-PBIs.[13,40] The ester functionalities of compound **1** did not hydrolyze and remained intact under these reaction conditions. Upon reacting **1** with an excess (8 equiv) of either 4-methoxyphenol or 4-*tert*-butylphenol at 95 °C, the corresponding 7,12-di-(4-methoxyphenoxy)-perylene monoimide diester **2** and 7,12-di-(4-*tert*-butylphenoxy)-perylene monoimide diester **3** were obtained in yields of ∼90% (Scheme 1). It is important to mention that the reaction was completely regiospecific and we did not even find traces of other possible regioisomers. Moreover, no tri-phenoxy substitution was observed under these conditions. The regiospecific substitution at the 7,12-positions in compounds **2** and **3** were confirmed unambiguously by NMR measurements, as discussed in detail in the next section.

These disubstitution reactions are rather slow, and as a result, an excess of phenol (8 equiv), high temperature (95 °C), and long reaction time (∼20 h) are essential to achieve high yields. In our studies, we found that the temperature is a key parameter in this reaction. Lowering the temperature results in lower yields because of the increased amount of monosubstituted derivative. This is because the activation barrier for disubstitution is much higher as compared to that of the monosubstitution. Therefore, by lowering the reaction temperature to 65 °C, we were able to obtain monosubstituted compound 7-(4-methoxyphenoxy)-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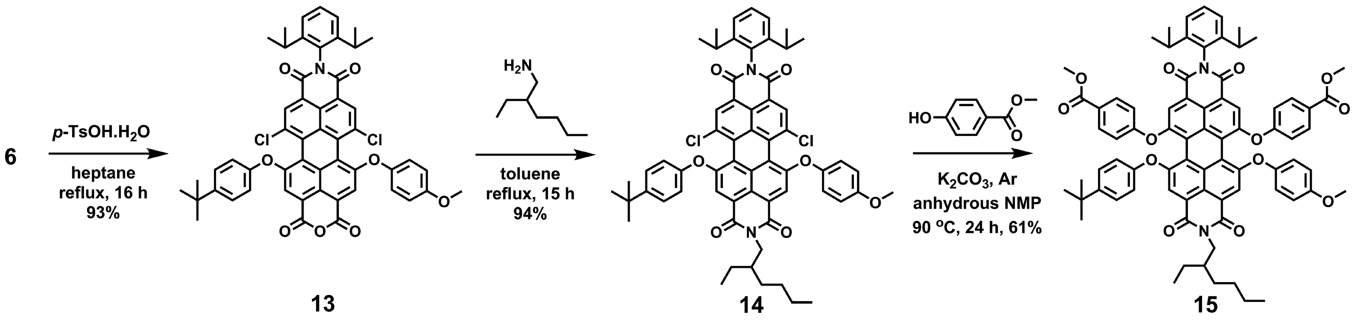
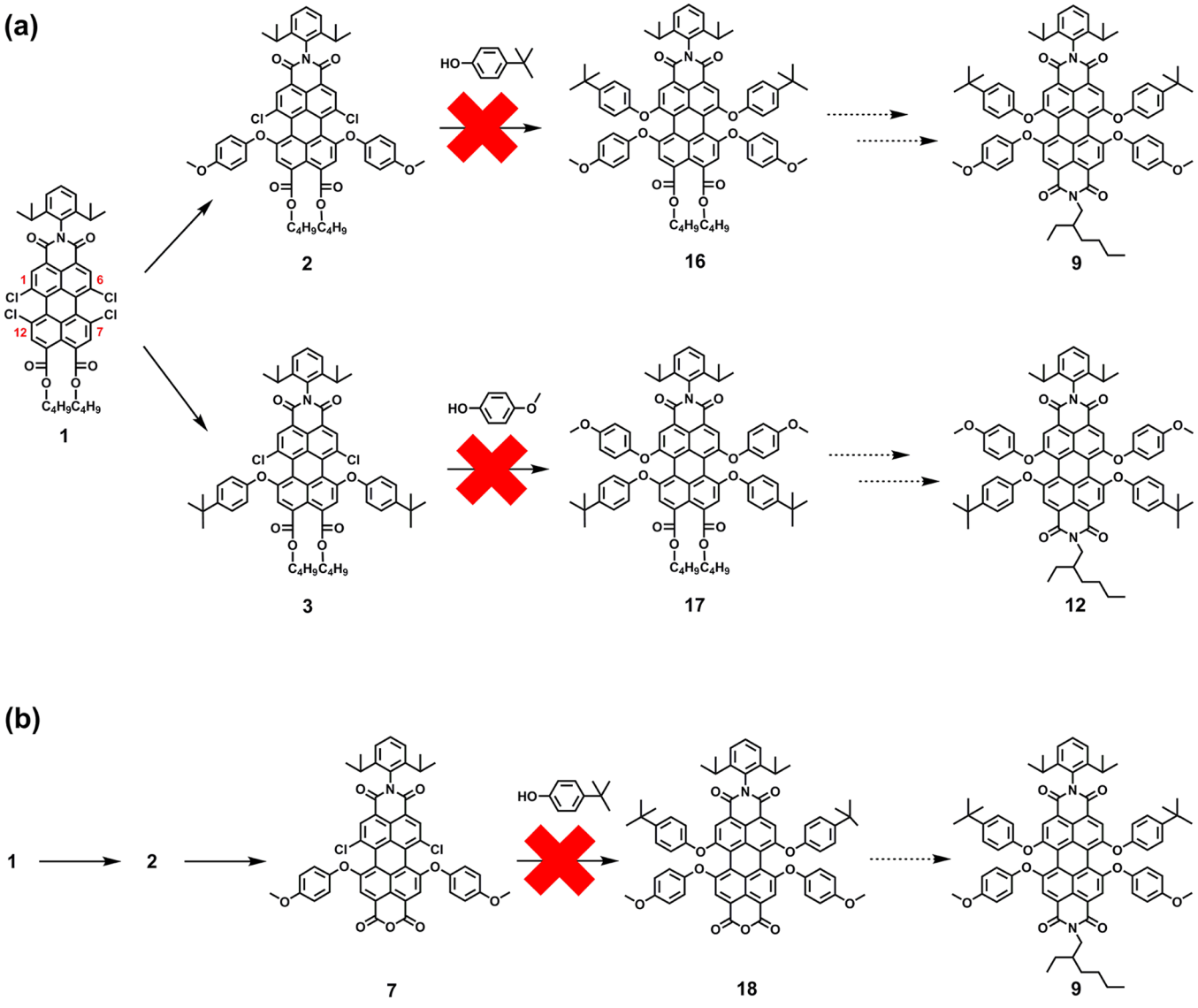
**Scheme 3. Synthesis of 1,6,7,12-Tetraphenoxyperylene Bisimide 15 Consisting of Five Different Substituents**




**Scheme 4. Investigation of Two Alternate Synthetic Routes (a) and (b) To Obtain 1,6,7,12-Tetraphenoxy-PBI Regioisomers (9 and 12) from Compound 1**




perylene monoimide diester **4** in 90% yield. Again, the reaction was regiospecific, and no substitution at the 1-position was observed. The reactivity of the phenol is the main factor that determines the temperature needed for the mono- and disubstitution. For example, for the weakest nucleophile methyl 4-hydroxybenzoate, the reaction temperature had to be raised to 90 °C to obtain the monosubstituted product in high yield (compound **5**).

Next, the scope of this reaction was expanded to sequential mono- and disubstitution. For this, we reacted the monophenoxy derivative **4** with 4-*tert*-butylphenol to obtain compound **6** that has two different phenoxy groups at the two bay positions. It is important to emphasize that the



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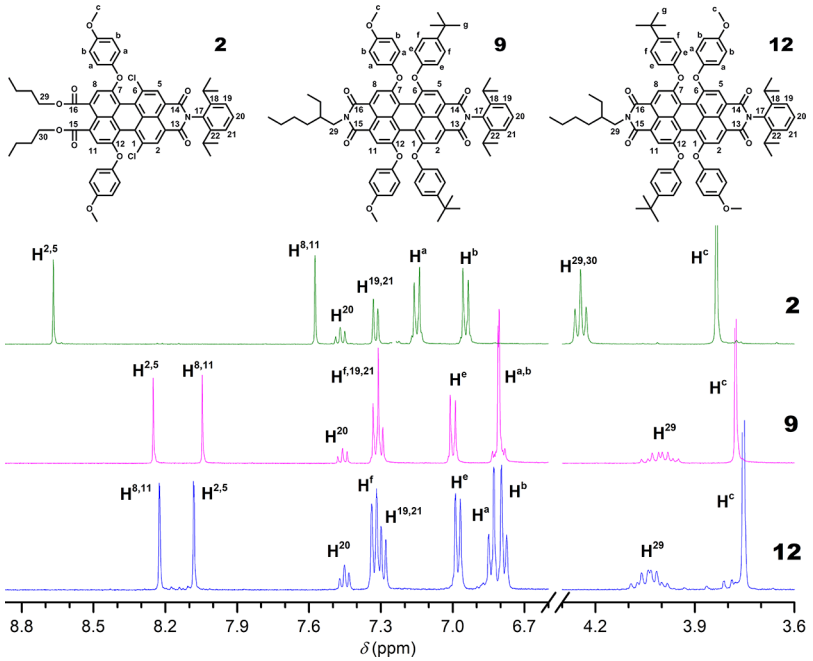


**Figure 3.** Selected region of $^1$H NMR (400 MHz) spectra of compounds **2**, **9**, and **12** with the assignment of signals.

unreacted reactants (especially phenols) are conveniently recovered because degradation of reactants does not occur due to the mild reaction conditions.

Scheme 2 depicts the facile synthetic methodology to extend the abovementioned regiospecific bis-substitution on compound **1** to obtain the novel 1,6,7,12-tetraphenoxy-PBI regioisomers **9** and **12** with two different phenoxy groups at bay positions and two different imide substituents. For this, the di-*n*-butylester moieties of 1,6-dichloro-7,12-diphenoxy derivatives **2** and **3** were converted to anhydride functionalities by treatment with an excess of *p*-TsOH·$H_2O$ in refluxing *n*-heptane. This reaction resulted in corresponding perylene monoimide monoanhydride derivatives **7** and **10** in ∼95% yield. Imidization of these compounds with 2-ethyl-1-hexylamine in refluxing toluene gave the corresponding unsymmetrically imide-substituted PBIs **8** and **11** in almost quantitative yields. It has to be emphasized that this is the first synthesis of 1,6-dichloro-7,12-diphenoxy-PBIs. The conversion of the di-*n*-butylester group to an imide was necessary to activate the 1,6-positions so that the remaining two 1,6-bay chlorines can also be substituted. This substitution was achieved by reactions with either 4-*tert*-butylphenol or 4-methoxyphenol in the presence of $K_2CO_3$ in anhydrous NMP to obtain tetraphenoxy derivatives **9** and **12**, respectively. For this reaction, we observed exchange of phenols at higher temperatures and longer reaction times.[48,52] Therefore, careful optimization of the reaction temperature and time was required to obtain good yields. It is important to note that compounds **9** and **12** are the two regioisomers in which the location of 4-methoxyphenoxy- and 4-*tert*-butylphenoxy groups has been reversed with respect to the imide groups. The successful synthesis of regioisomers **9** and **12**, starting from precursor **1** by reversing the order of bay-substitution, clearly shows that the procedure is robust and provides excellent control over the substitution pattern.

We further extended this sequential substitution-based approach to synthesize new PBI **15** bearing five different substituents, as depicted in Scheme 3. For this, the same synthetic procedure was applied on 7,12-diphenoxy-derivative **6**, which already had two different phenoxy groups (namely, 4-methoxyphenoxy and 4-*tert*-butylphenoxy) in the bay region. Acid-catalyzed removal of butyl esters followed by imidization with 2-ethyl-1-hexylamine yielded novel 7,12-diphenoxy-PBI **14** in excellent yield. Reaction of this PBI **14** with (4-methoxycarbonyl)phenol under standard conditions substituted the last two chlorines to provide 1,6,7,12-tetraphenoxy-PBI **15**. It should be noted that by lowering the reaction temperature, a single substitution of the third bay substituent is possible, but this substitution would not be regiospecific. This lack of regiospecificity currently prevents an efficient synthesis of perylenes bearing six independent substituents.

**Alternate Approaches To Achieve Unsymmetrical PBIs.** We have also investigated the practicality of two additional synthetic routes to obtain unsymmetrically substituted PBIs **9** and **12** from starting compound **1** as depicted in Scheme 4. In the first approach, we attempted to carry out subsequent phenoxy substitutions at the 7,12- and 1,6-bay-positions of 1,6,7,12-tetrachloro-perylene monoimide diester **1**. For this, 7,12-diphenoxy derivatives **2** and **3** were reacted with 4-tert-butylphenol and 4-methoxyphenol, respectively, under various reaction conditions (Scheme 4a). However, in all cases, the desired products (**16** and **17**) could not be obtained. Instead, we always observed an uncontrollable exchange of 7,12-phenoxy groups along with the phenoxy substitution at the 1,6-postions, and as a result, the reactions always produced a mixture of several phenoxy-substituted derivatives. These results further verify that the conversion of ester groups into an imide group to activate the 1,6-bay positions prior to phenoxy substitution is necessary because only then uncontrollable phenoxy exchange is suppressed.

In the second approach, we attempted to carry out 4-*tert*-butylphenoxy substitution at the 1,6-bay positions of 1,6-dichloro-7,12-di-(4-methoxyphenoxy)-perylene monoanhydride monoimide **7** using a number of reaction conditions. The rationale behind this approach was based on the assumption that the electron-deficient anhydride group will


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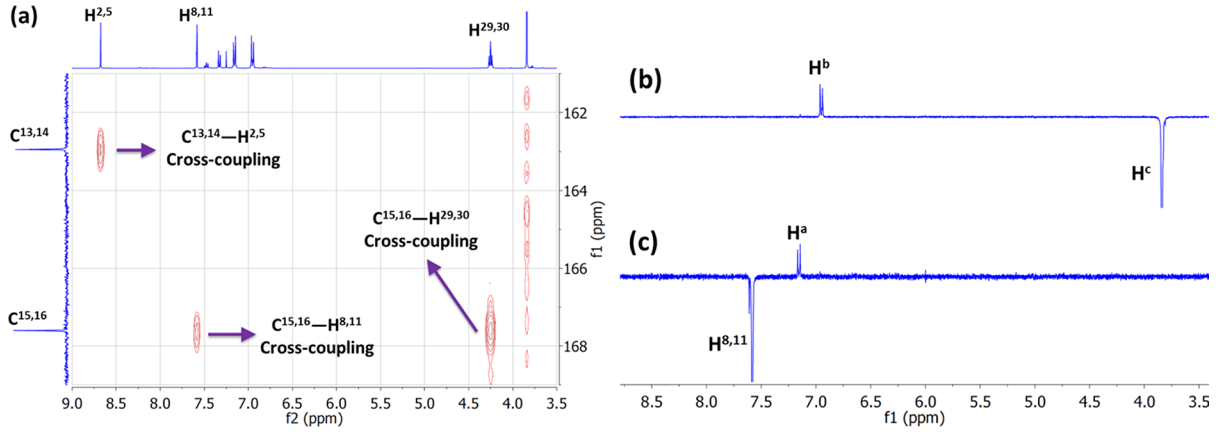


**Figure 4.** (a) Selected region of the $^{1}H-^{13}C$ HMBC spectrum of compound **2**; (b, c) 1D NOESY spectra of compound **2** showing through-space coupling between $H^c-H^b$ and $H^a-H^{8,11}$ respectively.

provide enough activation to the C-1 and C-6 positions. As a result, this will eventually allow the desired subsequent phenoxy substitution at the 1,6-positons. However, in this case also, the desired product **18** could not be obtained. Instead, all the reactions produced unrecognizable perylene derivatives, which did not show any mobility on the TLC plate. This fact indicated that the obtained derivatives contain a strongly polar group, which may have been generated due to nucleophilic attack of the phenol on the anhydride group.

**Structure Elucidation by 1D- and 2D-NMR Spectroscopy.** The regiospecific monophenoxy substitution at the 7-position and regiospecific bisphenoxy substitution at the 7,12-positions in compounds **2**, **3**, **4**, and **6** were confirmed unambiguously by a series of systematic 1D- and 2D-NMR measurements, namely, $^{1}H$, $^{13}C$, $^{13}C$-APT, $^{1}H-^{1}H$ COSY, $^{1}H-^{13}C$ HSQC, $^{1}H-^{13}C$ HMBC, $^{1}H-^{1}H$ NOESY, and homonuclear *J*-resolved spectroscopy (see Section 3 in the Supporting Information for detailed characterization). Subsequently, these experiments were also extended to verify the final substitution pattern in tetraphenoxy-PBI derivatives **9**, **12**, and **15**.

A selected region of $^{1}H$ NMR spectra of compounds **2**, **9**, and **12** is shown in Figure 3 with the assignment of signals to the various protons. As expected, compounds **9** and **12**, which are regioisomers, produced very similar $^{1}H$-NMR spectra. However, minor differences can be easily noticed. For example, the signals of $H^a$ and $H^b$ protons of 4-methoxyphenoxy groups (at ~6.8 ppm) are relatively separated in the case of compound **12**, whereas these signals are completely merged in compound **9**.

The crucial evidence for the proposed regiospecific substitutions was obtained by $^{1}H-^{13}C$ HMBC experiments. For example, for compound **2**, the $^{1}H-^{13}C$ HMBC spectrum clearly showed the long-range cross-coupling of ester carbonyl carbons $C^{15}$ and $C^{16}$ with perylene core protons $H^{11}$ and $H^{8}$ (Figure 4a). Similarly, the imide carbonyl carbons $C^{13}$ and $C^{14}$ exhibited cross-coupling with perylene core protons $H^{2}$ and $H^{5}$. The signals of ester carbonyl carbons ($C^{15}$ and $C^{16}$) and the imide carbonyl carbons ($C^{13}$ and $C^{14}$) were unambiguously identified based on the fact that the ester carbonyl carbons also exhibited long-range cross-coupling with butyl-chain protons $H^{29}$ and $H^{30}$. The final confirmation to the proposed structural assignment was provided by 1D $^{1}H-^{1}H$ NOESY experiments (Figure 4b,c) in which through-space cross-coupling between $H^c-H^b$ and $H^a-H^{8,11}$ was clearly observed. The structures of all other compounds have also been elucidated in the same manner and discussed in detail in the Supporting Information.

**Electrochemical Properties.** Cyclic voltammetry (CV) has been performed on the selected compounds **1**, **2**, **4**, **8**, **9**, and **12**. The obtained redox potentials versus $Fc/Fc^+$ in dichloromethane together with calculated HOMO and LUMO energy levels versus vacuum are listed in Table 1. In this study, we have included tetrachloro-perylene monoimide diester **1** and tetrachloro-perylene bisimide (PBI-$Cl_4$) as the reference compounds to understand the impact of sequential phenoxy substitution on the electron-accepting nature of the perylene chromophore.

**Table 1. Redox Potentials (vs $Fc/Fc^+$) and Electronic Energy Levels (vs Vacuum) of Selected Perylene Derivatives**[a]

| compound | $E_{1red}$ | $E_{2red}$ | $E_{1ox}$ | $E_g$[b] (eV) | $E_{LUMO}$[c] (eV) | $E_{HOMO}$[d] (eV) |
|---|---|---|---|---|---|---|
| **1** | −0.95 | −1.13[e] | [f] | 2.35 | −3.85 | −6.20 |
| **4** | −1.13 | −1.28[e] | [f] | 2.21 | −3.67 | −5.88 |
| **2** | −1.24 | −1.54 | [f] | 2.15 | −3.56 | −5.71 |
| PBI-$Cl_4$[g] | −0.79 | −1.00 | [f] | 2.25 | −4.01 | −6.27 |
| **8** | −1.03 | −1.25 | [f] | 2.06 | −3.77 | −5.83 |
| **9** | −1.25 | [f] | +0.78 | 2.02 | −3.55 | −5.57 |
| **12** | −1.24 | [f] | +0.78 | 2.02 | −3.56 | −5.58 |

[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]Optical band gap calculated using the equation $E_g = hc/\lambda_{ae} \approx 1240/\lambda_{ae}(nm)$ where $\lambda_{ae}$ denotes the absorption edge wavelength in nm obtained from the offset wavelength derived from the low energy absorption band.[53] [c]Estimated vs vacuum level from $E_{LUMO} = -(E_{1red} + 4.8$ eV). [d]Estimated from $E_{HOMO} = E_{LUMO} - E_g$. [e]Quasi-reversible (peak potential is reported). [f]Not observed. [g]*N,N'*-Di-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene bisimide (the structure is mentioned in the Supporting Information).

In general, the PBI dyes are good *n*-type semiconductors that exhibit two reversible reduction waves corresponding to the formation of the radical anion and dianion.[1] In this series of compounds, the tetrachloro-perylene monoimide diester **1** exhibits a first reduction potential at −0.95 V. The placement of one and two phenoxy groups in the bay region (compounds **4** and **2**) moves the reduction potential to −1.13 and − 1.24, respectively. This variation shows that the



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electron deficiency noticeably decreases even by the presence of one phenoxy group and it further decreases by the second phenoxy substitution.

The tetrachloro-perylene bisimide (PBI-$Cl_4$) is the most electron-deficient compound in the series due to the presence of two strong electron-withdrawing imide groups at the peri-positions. For this, the first reduction occurs at the least negative potential (−0.79 V). It moves significantly to a more negative potential (−1.03 V) for compound **8** that has two phenoxy groups at the 7- and 12-bay positions. This shift of 0.24 V clearly shows that the presence of two phenoxy substituents already exerts a strong negative impact on the electron deficiency of PBIs. For compound **9**, as expected, the four phenoxy substituents further move the reduction potential to −1.25 V. There are two observations worth noting in these results. First, the reduction potential increases systematically in a stepwise manner upon moving from PBI-$Cl_4$ to compound **8** and finally to compound **9** by ∼0.23 V for each step. In this way, these results demonstrated that this synthetic approach can be used to fine-tune the electronic properties of the perylene bisimide chromophore. Second, the tetraphenoxy regioisomers **9** and **12** exhibit identical values of both the reduction and oxidation potentials. This was expected considering that interchanging phenoxy groups should not have any overall effect on the electrochemical properties of the dye.

Figure 5 depicts the experimentally obtained HOMO and LUMO levels of the studied perylene derivatives **1**, **2**, **4**, **8**, **9**, **12**, and PBI-$Cl_4$. Important to notice here is that the sequential phenoxy substitution has a clear effect on both HOMO and LUMO levels. For example, the HOMO and LUMO levels of PBI **8**, which has two phenoxy substituents, are significantly higher in energy as compared to the corresponding levels of PBI-$Cl_4$. Upon moving to PBI **9**, which has four phenoxy substituents, the energies of HOMO and LUMO levels move further up. Thanks to this effect, the sequential substitution approach provides a simple and viable means to control the HOMO−LUMO energies of perylene dyes.

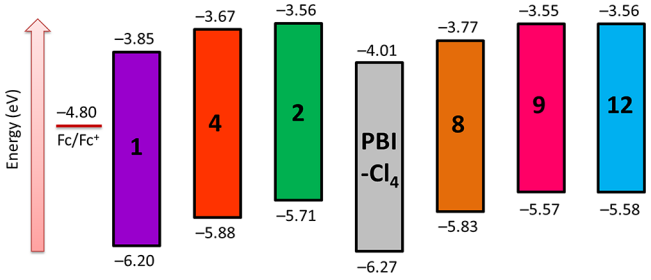


**Figure 5.** HOMO and LUMO levels of synthesized perylene derivatives against vacuum.

**Absorption and Emission Properties.** The synthesized perylene derivatives are based on three different phenoxy groups, that is, 4-methoxyphenoxy, 4-*tert*-butylphenoxy, and 4-methoxycarbonylphenoxy. Among them, the 4-methoxyphenoxy group is special because of its capability to donate an electron to the photoexcited perylene and quench fluorescence.[40,54] Therefore, absorption and emission studies were conducted on the synthesized compounds to investigate the effect of sequential structural modification on the photophysical properties. The normalized absorption and emission spectra of compounds **1**, **2**, **4**, **8**, **9**, and **12** in toluene are shown in Figure 6, and the relevant spectroscopic data are summarized in Table 2. To assess the magnitude of photoinduced charge transfer, three other compounds **3**, **5**, and **11** were used as model compounds. They make a good set of model compounds for this study as they carry relatively electron-poor 4-*tert*-butylphenoxy or 4-methoxycarbonylphenoxy groups, which do not show any photoinduced charge transfer even in highly polar solvents.[40]

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 observed for these compounds in their optical properties depending on the functionalization either at the peri or bay positions. The perylene monoimide diester **1**, which carries four chlorine atoms at the bay positions, has the most blue-shifted absorption ($\lambda_{max}$ = 496 nm) and emission ($\lambda_{max}$ = 530 nm) spectra. Both absorption and emission spectra clearly respond to the phenoxy substitution and exhibit a systematic bathochromic shift upon moving from compound **1** to **9** (Figure 6).

Surprisingly, a striking effect of the sequential 4-methoxyphenoxy substitution has been observed on the fluorescence quantum yields and lifetimes. The perylenes, in general, exhibit high fluorescence quantum yields and long lifetimes as can be seen for compound **1** ($\varphi_f$ = 0.89 and $\tau_f$ = 4.86 ns). Substitution of one 4-methoxyphenoxy group (compound **4**) leads to a drastic decrease of both quantum yield and lifetime (Figure 7 and Table 2). Surprisingly, the presence of two 4-methoxyphenoxy groups (compound **2**) results in a significant recovery of both. The subsequent conversion of diester groups to an imide (compound **8**) again decreases the quantum yield and lifetime, which significantly recover in response to the two additional phenoxy substituents (compound **9**).

These modulations of fluorescence properties in response to the sequential functionalization are essentially due to the change in the magnitude of charge transfer rates between the 4-methoxyphenoxy group and the photoexcited perylene moiety. This presumption of photoinduced charge transfer is

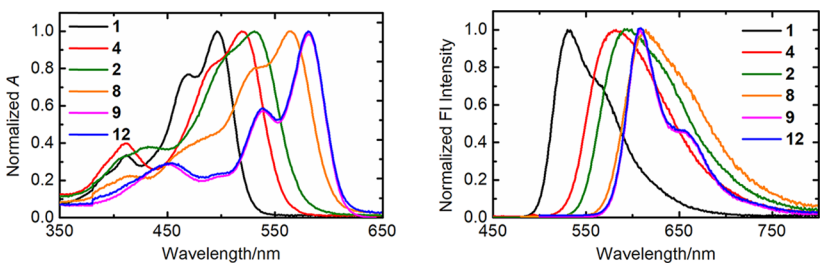


**Figure 6.** (Left) Normalized UV/vis absorption and (right) emission spectra in toluene.



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**Table 2. Optical Properties of the Selected Compounds 1, 2, 4, 8, 9, and 12 in Toluene**

| compound | $\lambda_{abs}$ (nm) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $\lambda_{em}$ (nm) | stokes shift ($cm^{-1}$) | $\Phi_f$[a] | $\tau_f$ (ns)[b] |
|---|---|---|---|---|---|---|
| **1** | 496 | 34500 | 530 | 1293 | 0.89 | 4.86 |
| **4** | 519 | 26000 | 582 | 2086 | 0.12 (0.92)[c] | 1.01 (6.09)[c] |
| **2** | 531 | 24900 | 599 | 2138 | 0.55 (0.79)[c] | 5.17 (6.42)[c] |
| **8** | 565 | 42300 | 614 | 1412 | 0.13 (0.72)[c] | 0.56 (6.73)[c] |
| **9** | 581 | 60300 | 608 | 764 | 0.58 | 5.32 |
| **12** | 581 | 62000 | 608 | 764 | 0.57 | 5.25 |

[a]Fluorescence quantum yield. [b]Fluorescence lifetime. [c]The values in parenthesis are from the corresponding model compound **3**, **5**, or **11**.

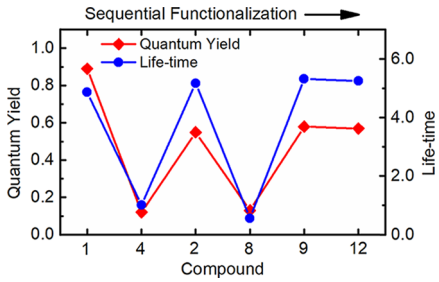


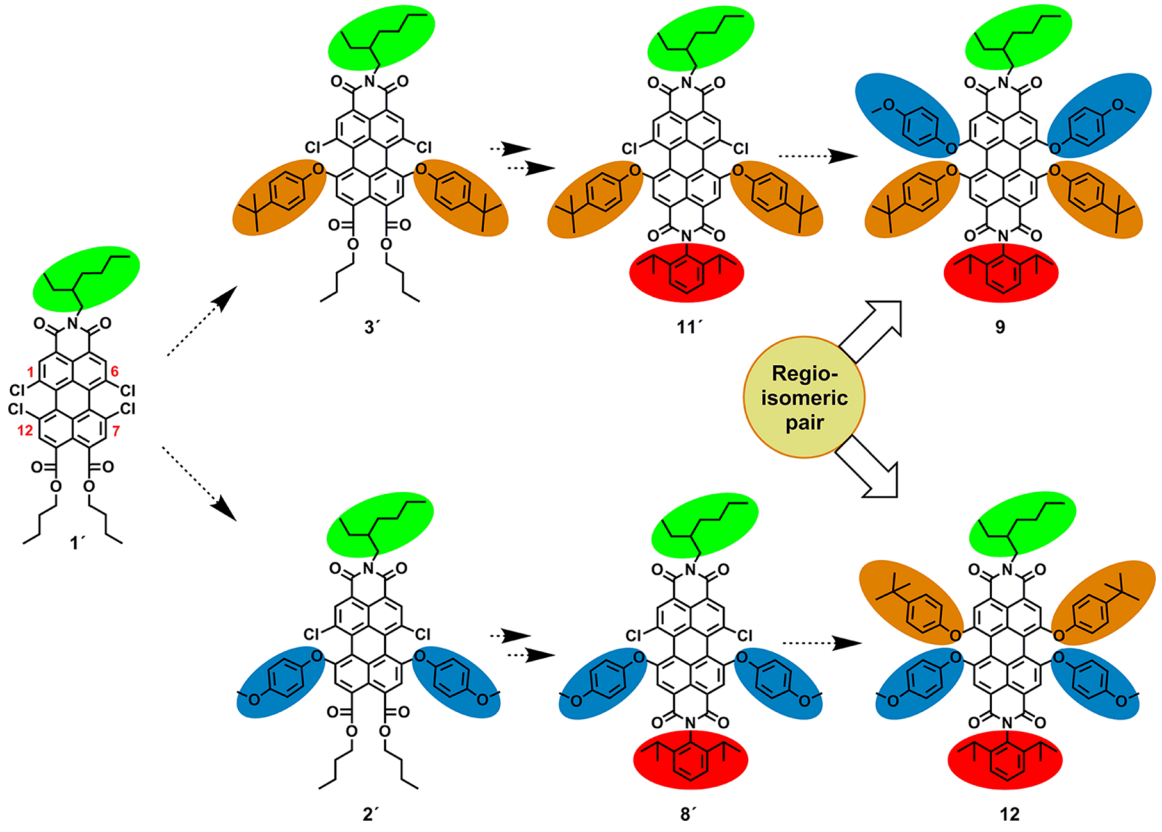

**Figure 7.** Modulation of the fluorescence properties in response to sequential functionalization.

well supported by the previous studies[54,40] and also by the fact that the corresponding model compounds (**3**, **5**, and **11**) all exhibit high fluoresce quantum yields ($\varphi_f$ = 0.72−0.92) and long lifetimes ($\tau_f$ = 6−7 ns). The change in the magnitude of charge transfer upon sequential phenoxy substitution can be clearly explained based on the change in the first reduction potentials as observed in the cyclic voltammetry study. For example, compound **4**, which has only one 4-methoxyphenoxy group, is relatively more electron-deficient ($E_{1red}$ = −1.13 V) and, as a result, exhibits more efficient charge transfer as compared to compound **2** ($E_{1red}$ = −1.24 V) that carries two 4-methoxyphenoxy groups. This shows that photoinduced charge transfer in perylene-based systems is highly sensitive to small variations in the electron deficiency of the perylene core. Also, since this sequential phenoxy substitution is capable of inducing those small variations, the bay substitution strategy presented here offers an efficient way to control the photophysical processes in perylene dyes.

## DISCUSSION

The synthesis described in this work started from 1,6,7,12-tetrachloroperylene monoimide diester **1**, a compound that has the 2,6-diisopropylphenyl group at the imide position. However, any other imide group can be used aside from the 2,6-diisopropylphenyl group, and the resultant perylene monoimide diester derivative will react exactly in the same

**Scheme 5. Alternate Possible Route To Synthesize Regioisomers 9 and 12 Starting from Compound 1′ by the Reversed Bay Substitution Approach**



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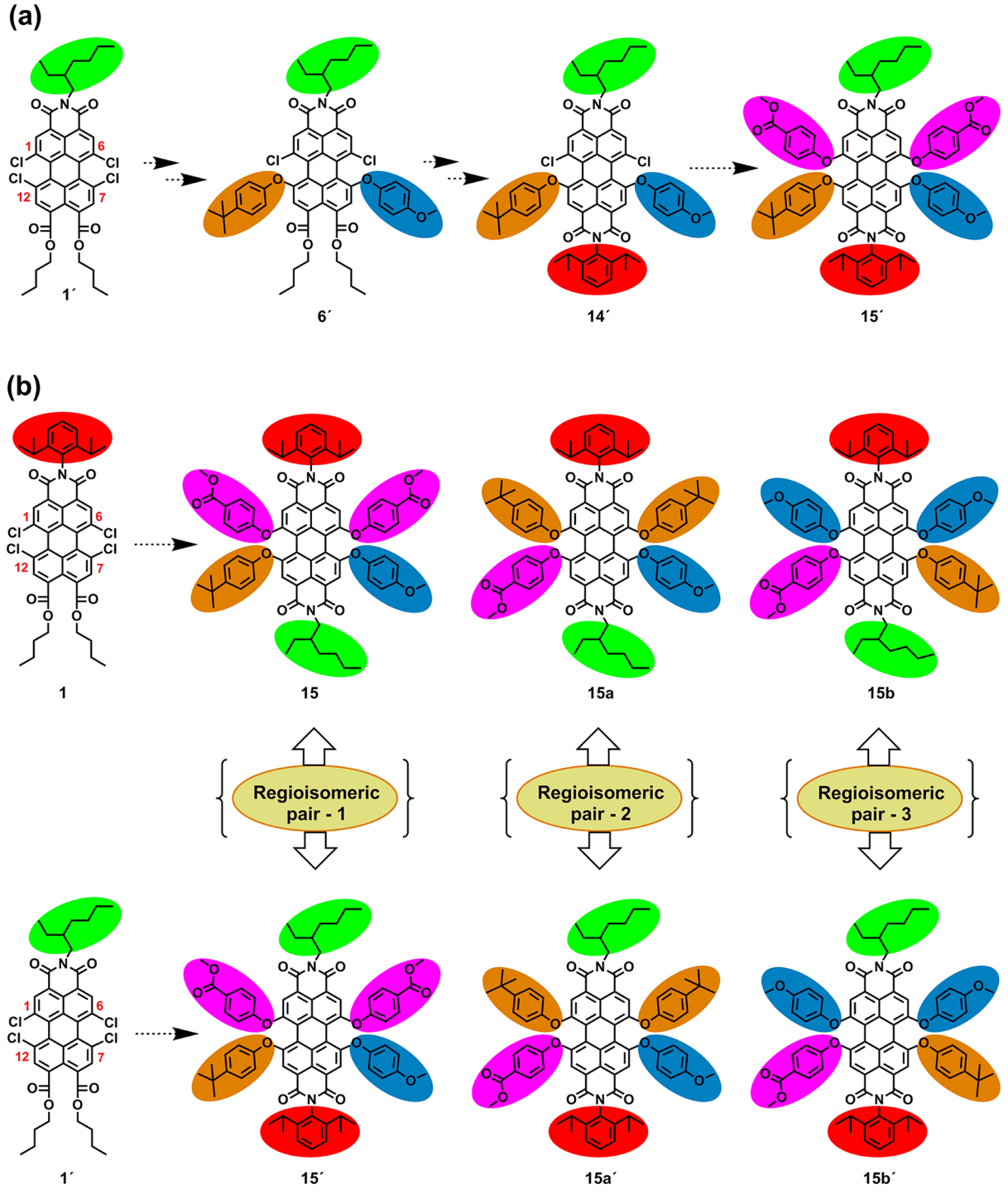
**Scheme 6.** (a) Accessibility of Regioisomer 15′ from Compound 1′ Using the Reversed Imide-Substitution Approach; (b) Synthetic Approach To Access Three Pairs of Regioisomers of PBIs with Five Different Substituents




manner as compound **1**. This is because the nature of the imide group does not affect the electronic structure of the perylene core and thereby its reactivity pattern.[1] This implies that the two PBI regioisomers **9** and **12**, prepared herein from compound **1** by reversing the order of the bay substituents, can also be synthesized equally well by starting the synthesis with the corresponding 2-ethyl-1-hexyl-substituted perylene monoimide diester **1′** using the same procedure (Scheme 5). Important to note here is that the pair of two regioisomers **9** and **12** can also be synthesized without reversing the order of bay substitution. For that, the synthesis of one of the regioisomers (either **9** or **12**) has to be started from compound **1** and synthesis of the other isomer from compound **1′**, that is, by reversing the order of imide-substituents while keeping the order of bay substitution the same. This approach of reversing the order of imide-substitution is clearly more practical than reversing the sequence of bay substitution when the reactivity of the two phenols is very different. This is because in this approach, there is no need to optimize the conditions for bay substitution performed two times separately.



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Similarly, for compound **15**, which has five independent substituents, the other regioisomer **15′** (Scheme 6a) can be obtained most easily by reversing the order of imide attachment, that is, by starting the synthesis with the corresponding 2-ethyl-1-hexyl-substituted perylene monoimide diester **1′** while keeping the order of bay substituents and reaction conditions exactly the same as used for obtaining compound **15** (Scheme 6a). Regarding the PBIs with five independent substituents, it should be noted that in total, six compounds (three pairs of regioisomers) containing two different imides and three different bay substituents are accessible using the reversed imide-substitution methodology (Scheme 6b). Compound **15** has already been synthesized starting from **1**, and the accessibility of its regioisomer **15′** has been shown in Scheme 6a starting from **1′**, that is, by reversed imide substitution. Similarly, once the synthesis of compounds **15a** and **15b** is developed starting from compound **1**, their corresponding regioisomers **15a′** and **15b′** are accessible starting from compound **1′** using the identical bay substitution pattern and reaction conditions.

Importantly, the synthesis of these three pairs of regioisomers can also be imagined by reversed bay substitution. Following this approach, compounds **15′**, **15a′**, and **15b′** have to be synthesized from compound **1** by attaching identical substituents at positions 7 and 12 and adding the different substituents at positions 1 and 6 later on. Subsequent substitution at positions 1 and 6 has not been demonstrated in this work. However, since each subsequent bay substitution has a higher activation energy, there is no obvious reason why such a procedure would not work. However, since the last bay substitution requires harsher reaction conditions, exchange of phenols and thus lower yields are anticipated for this approach. To minimize the exchange of phenols, the fluoride-assisted bay chlorine substitution-based approach, recently developed by Fernández Lázaro et al.,[33] can be used as a potential option. This may be highly successful to carry out subsequent substitution at positions 1 and 6 considering its moderate reaction conditions (THF-reflux), thus minimizing the phenol exchange.

Finally, it should be noted that the sequential functionalization approach used in this work has the potential to obtain PBIs even with six different substituents. This however requires a regioselective substitution of the third bay substituent, either at the 1- or 6-position. It is anticipated that by using sterically distinct substituents at the 7- and 12-positions, such regioselectivity can be accomplished. Obtaining PBIs with six different substituents, by achieving full control over the substitution pattern of tetra-bay-substituted PBIs, may therefore be regarded as the next synthetic challenge in perylene chemistry.

## CONCLUSIONS

We have achieved regiospecific 7-mono- and 7,12-bisphenoxy substitution at the bay positions of 1,6,7,12-tetrachloroperylene monoimide diester in very high yields using mild reaction conditions. Subsequently, this regiospecificity has been utilized to devise an efficient and convenient synthetic approach for the synthesis of novel unsymmetrically imide- and bay-substituted perylene bisimides with up to five different substituents, that is, two at the imide positions and up to three at the bay positions. This is a major step forward in perylene chemistry as previous protocols were capable of producing perylene bisimide derivatives with a maximum of three different substituents. This methodology has four additional salient features from the synthetic perspective. First, it gives 7,12-disubstituted perylene bisimides, which is unprecedented. Second, this methodology is versatile and can easily be extended to other functional imide and bay substituents. Third, the sequential substitutions at the bay and imide positions can be achieved with good control, which opens the way to prepare all regioisomers containing the same bay substituents. Lastly, this approach paves the way for perylene bisimides with six independent substituents.

The sequential structure modifications at the bay and peri positions impose a systematic change in the photophysical and electrochemical properties. In this way, the synthetic methodology described in this manuscript provides a simple, efficient, and viable tool to achieve precise control over the optoelectronic characteristics of photofunctional perylene dyes. This approach will eventually enable the synthesis of more complex covalent and supramolecular architectures (e.g., multichromophoric systems and dendrimers) based on perylene bisimide dyes.

Current research is directed toward regioselective substitution of the third (and fourth) bay chlorine and expanding the palette of bay substituents. Incorporation of functionality in the imides, to capitalize on the specific imide pattern, and attaching electronically inequivalent substituents at the bay positions are additional research directions that will be explored.

## EXPERIMENTAL SECTION

**Materials.** All the reagents utilized in the synthesis were purchased from commercial suppliers and used as received unless otherwise stated. The toluene and NMP used in the phenoxy functionalization reactions were of anhydrous grade. All reactions were conducted in an oil bath. The purification of the products was 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 a 400 MHz pulsed Fourier transform NMR spectrometer in either $CDCl_3$ or $CD_2Cl_2$ at temperature regulated at 25 °C. 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 $\mu$m). Typical measurement conditions were as follows: 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 sheet as the working electrode, silver wire as the reference electrode, and a platinum wire as the counter electrode. The cell was connected to a computer-controlled potentiostat (CH Instruments Inc. 600D). Predried $CH_2Cl_2$ 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 ∼0.5 mM. Under these experimental conditions, the ferrocene oxidation was observed at 0.51 V. The potentials of all the reversible peaks are reported as $E_{1/2} = (E_p^a + E_p^c)/2$ in V versus $Fc/Fc^+$ and quoted to the nearest 0.01 V. The measurements were carried out at a 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 the following compounds as reference: perylene-


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3,4,9,10-tetracarboxylic tetramethylester ($\Phi_f$ = 0.95 in $CH_2Cl_2$) and *N*,*N*′-bis(1-hexylheptyl)-perylene-3,4,9,10-tetracarboxy bisimide ($\Phi_f$ = 0.99 in $CHCl_3$).[55] Fluorescence lifetime measurements were performed after excitation at 400 nm on a Lifespec-ps fluorescence spectrometer from Edinburgh Instruments. The time-correlated fluorescence was analyzed by an exponential tail fit with F900 Lifespec software.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7,12-di-(4-methoxyphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (2).** A dry 250 mL round-bottom flask was charged with 4-methoxyphenol (0.85 g, 6.85 mmol), anhydrous potassium carbonate (1.42 g, 10.25 mmol), 18-crown-6 (2.71 g, 10.25 mmol), and anhydrous toluene (70 mL) under an argon atmosphere. The resultant mixture was stirred for 20 min at room temperature. Subsequently, *N*-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene monoimide dibutylester **1** (0.70 g, 0.85 mmol) was added. The reaction was continued for 20 h at 95 °C in an oil bath and then allowed to cool down to room temperature. More toluene (70 mL) was added, and the resultant solution was extracted with water (3 × 100 mL). The organic phase was collected, and toluene was evaporated under reduced pressure. The solid residue was chromatographed on silica, eluting with 2:1 $CH_2Cl_2$−hexane to afford the desired product **2** (0.77 g, 91%) as a dark red crystalline solid. Mp 152−154 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.67 (s, 2H), 7.58 (s, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 4.25 (t, *J* = 6.4 Hz, 4H), 3.84 (s, 6H), 2.76−2.66 (m, 2H), 1.71−1.62 (m, 4H), 1.40−1.29 (m, 4H), 1.15 (d, *J* = 6.8 Hz, 12H), 0.91 ppm (t, *J* = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 167.60, 162.95, 157.14, 155.97, 147.04, 145.63, 134.88, 133.78, 133.24, 133.01, 132.56, 130.79, 130.43, 129.66, 124.26, 124.08, 121.73, 120.61, 117.98, 117.77, 115.35, 115.15, 65.71, 55.66, 30.38, 29.18, 23.97, 19.13, 13.68 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{58}H_{53}Cl_2NO_{10}$, 993.3047; found, 993.3083.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7,12-di-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (3).** The compound was prepared as per the procedure described for compound **2** using 4-*tert*-butylphenol (0.88 g, 5.86 mmol), anhydrous potassium carbonate (1.01 g, 7.30 mmol), 18-crown-6 (1.93 g, 7.30 mmol), *N*-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene monoimide dibutylester **1** (0.60 g, 0.73 mmol), and anhydrous toluene (60 mL). The crude product was chromatographed on silica, eluting with 1:1 $CH_2Cl_2$-−hexane to afford the desired product **3** (0.68 g, 89%) as an orange-red crystalline solid. Mp 198−200 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.64 (s, 2H), 7.67 (s, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 4H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 4H), 4.29−4.22 (m, 4H), 2.74−2.66 (m, 2H), 1.71−1.63 (m, 4H), 1.40−1.31 (m + singlet of *tert*-butyl groups, 22H), 1.14 (d, *J* = 6.8 Hz, 12H), 0.90 ppm (t, *J* = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 167.61, 162.91, 155.35, 151.37, 148.34, 145.62, 134.98, 133.92, 133.19, 132.97, 132.45, 130.72, 130.42, 129.65, 126.92, 124.23, 124.07, 120.65, 119.73, 118.59, 118.03, 115.89, 65.67, 34.51, 31.42, 30.36, 29.17, 23.97, 19.09, 13.71 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{64}H_{65}Cl_2NO_8$, 1045.4087; found, 1045.4110.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6,12-trichloro-7-(4-methoxyphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (4).** A mixture of 4-methoxyphenol (0.42 g, 3.41 mmol), anhydrous potassium carbonate (0.59 g, 4.27 mmol), and 18-crown-6 (1.13 g, 4.27 mmol) was taken in a dried round-bottom flask. Subsequently, anhydrous toluene (70 mL) was added. The resultant mixture was stirred for 20 min at room temperature under an argon atmosphere. Thereafter, *N*-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene monoimide dibutylester **1** (0.70 g, 0.85 mmol) was added. The temperature of the reaction was raised to 65 °C and stirred for another 16 h. After being cooled to room temperature, more toluene (70 mL) was added, and the resultant solution was extracted with water (3 × 100 mL). The organic phase was collected, and toluene was evaporated. The solid residue was chromatographed on silica (2:1 $CH_2Cl_2$−hexane) to afford the desired product **4** (0.70 g, 90%) as a red crystalline solid. Mp 162−167 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.68 (s, 1H), 8.67 (s, 1H), 8.08 (s, 1H), 7.65 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 2.78−2.68 (m, 2H), 1.86−1.76 (m, 2H), 1.74−1.66 (m, 2H), 1.54−1.46 (m, 2H), 1.40−1.32 (m, 2H), 1.20−1.12 (m, 12H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.91 ppm (t, *J* = 7.2 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 167.28, 167.15, 162.74, 157.29, 155.72, 146.83, 145.65, 145.59, 134.57, 134.48, 134.37, 133.98, 133.40, 133.03, 132.18, 131.60, 130.62, 130.45, 130.23, 129.95, 129.77, 126.47, 124.14, 123.93, 122.07, 121.71, 120.99, 120.55, 119.44, 115.24, 115.17, 66.06, 65.86, 55.67, 30.56, 30.37, 29.20, 23.98, 19.20, 19.14, 13.77, 13.68 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{51}H_{46}Cl_3NO_8$, 905.2289; found, 905.2310.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6,12-trichloro-7-(4-methoxycarbonylphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (5).** Prepared as per the procedure described for compound **4** from methyl 4-hydroxybenzoate (0.30 g, 1.97 mmol), anhydrous potassium carbonate (0.34 g, 2.44 mmol), 18-crown-6 (0.65 g, 2.44 mmol), *N*-(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene monoimide dibutylester **1** (0.20 g, 0.24 mmol), and anhydrous toluene (20 mL). The reaction mixture was stirred for 18 h at 90 °C. The crude product was chromatographed on silica first with a 2:1 $CH_2Cl_2$−hexane mixture to remove unreacted starting compound **1** and subsequently with 4:1 $CH_2Cl_2$−hexane to afford the desired product **5** (0.18 g, 79%) as an orange crystalline solid. Mp 132−134 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.68 (s, 1H), 8.64 (s, 1H), 8.10 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 4.37 (t, *J* = 6.8 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 2.75−2.65 (m, 2H), 1.87−1.78 (m, 2H), 1.75−1.66 (m, 2H), 1.54−1.46 (m, 2H), 1.42−1.34 (m, 2H), 1.20−1.12 (m, 12H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.92 ppm (t, *J* = 7.2 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 167.04, 167.01, 166.08, 162.61, 157.83, 153.41, 145.59, 134.90, 134.63, 134.42, 134.29, 133.29, 133.23, 133.17, 131.97, 131.94, 131.67, 131.21, 130.21, 130.12, 129.82, 129.36, 126.95, 126.72, 124.14, 123.88, 122.22, 121.42, 121.35, 120.84, 119.27, 116.87, 66.16, 66.06, 52.24, 30.56, 30.39, 29.20, 23.96, 19.21, 19.14, 13.77, 13.67 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{52}H_{46}Cl_3NO_9$, 933.2238; found, 933.2202.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7-(4-methoxyphenoxy)-12-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Dibutylester (6).** In an oven-dried round-bottom flask, a mixture of 4-*tert*-butylphenol (0.79 g 5.26 mmol), anhydrous potassium carbonate (0.73 g, 5.28 mmol), and 18-crown-6 (1.74 g, 6.60 mmol) was stirred for 20 min in anhydrous toluene (40 mL) at room temperature under an argon atmosphere. Subsequently, compound **4** (0.60 g, 0.66 mmol) was added, and the reaction mixture was stirred for an additional 16 h at a temperature of 95 °C. Thereafter, the reaction mixture was allowed to cool down to room temperature and was extracted with water (3 × 100 mL). The organic phase was collected, and toluene was evaporated under reduced pressure. The solid residue was washed with a 5:1 MeOH−$H_2O$ mixture to remove unreacted phenol. The final purification was done by column chromatography on silica (2:1 $CH_2Cl_2$−hexane) to afford the desired product **6** (0.51 g, 75%) as a dark red crystalline solid. Mp 164−166 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.66 (s, 1H), 8.65 (s, 1H), 7.66 (s, 1H), 7.58 (s, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 4H), 3.84 (s, 3H), 2.75−2.65 (m, 2H), 1.74−1.62 (m, 4H), 1.42−1.28 (m + singlet of *tert*-butyl group, 13H), 1.15 (d, *J* = 6.8 Hz, 12H), 0.94−0.86 ppm (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 167.60, 162.92, 157.14, 155.92, 155.40, 151.37, 148.35, 147.06, 145.63, 145.61, 134.94, 133.91, 133.79, 133.23, 133.20, 133.02, 132.97, 132.49, 130.76, 130.43, 129.66, 126.92, 124.25, 124.07, 121.71, 120.64, 119.75, 118.51, 118.02, 117.89, 115.82, 115.42, 115.16, 65.72, 65.66, 55.66, 34.52, 31.42, 30.39, 29.18, 23.98, 19.14, 19.09, 13.71, 13.69, ppm. MS



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(ESI-TOF): $[M]^+$ calculated for $C_{61}H_{59}Cl_2NO_9$, 1019.3567; found, 1019.3606.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7,12-di-(4-methoxyphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (7).** Compound **2** (0.29 g, 0.29 mmol) and *p*-TsOH·$H_2O$ (0.17 g, 0.89 mmol) were taken in *n*-heptane (25 mL). The mixture was stirred at reflux for 16 h. After cooling down to room temperature, heptane was evaporated on a rotavapor. The solid residue was suspended in methanol (50 mL), and subsequently water (30 mL) was added. The resultant precipitate was collected by filtration and washed a few times with water to collect the product (0.24 g, 95%) as a purple solid. Mp > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.74 (s, 2H), 8.14 (s, 2H), 7.49 (t, $J$ = 8.0 Hz, 1H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.8 Hz, 4H), 6.99 (d, $J$ = 8.8 Hz, 4H), 3.87 (s, 6H), 2.74−2.64 (m, 2H), 1.15 ppm (d, $J$ = 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 162.66, 159.33, 157.64, 157.24, 146.52, 145.55, 135.35, 133.53, 132.88, 132.58, 130.06, 129.87, 129.65, 124.44, 124.19, 121.82, 121.67, 120.30, 120.08, 119.39, 119.22, 115.63, 55.73, 29.25, 23.96 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{50}H_{35}Cl_2NO_9$, 863.1783; found, 863.1763.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-dichloro-7,12-di-(4-methoxyphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (8).** A 25 mL round-bottom flask was charged with compound **7** (150 mg, 0.17 mmol), 2-ethyl-1-hexylamine (45 mg, 0.35 mmol), and toluene (10 mL). The mixture was stirred at reflux for 16 h. Thereafter, toluene (10 mL) was added, and the resultant solution was extracted with water (3 × 30 mL). The organic phase was collected, and toluene was evaporated under reduced pressure. The resultant solid residue was purified by column chromatography on silica (2:1 $CH_2Cl_2$−hexane) to obtain the desired product **8** (166 mg, 98%) as a purple solid. Mp 224−226 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.72 (s, 2H), 8.15 (s, 2H), 7.47 (t, $J$ = 7.6 Hz, 1H), 7.33 (d, $J$ = 7.6 Hz, 2H), 7.17 (d, $J$ = 8.8 Hz, 4H), 6.98 (d, $J$ = 8.8 Hz, 4H), 4.12−3.98 (m, 2H), 3.86 (s, 6H), 2.75−2.66 (m, 2H), 1.90−1.82 (m, 1H), 1.40−1.28 (m, 8H), 1.15 (d, $J$ = 6.8 Hz, 12H), 0.92−0.82 ppm (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 163.37, 162.75, 157.39, 146.84, 145.58, 134.59, 133.42, 132.49, 132.45, 130.26, 129.76, 124.52, 124.36, 124.12, 121.74, 121.34, 118.22, 117.77, 117.69, 115.48, 55.69, 44.54, 38.12, 29.22, 28.79, 28.72, 24.04, 23.97, 23.04, 14.08, 10.59 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{58}H_{52}Cl_2N_2O_8$, 974.3101; found, 974.3059.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-di-(4-*tert*-butylphenoxy)-7,12-di-(4-methoxyphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (9).** Weighed amounts of PBI **8** (100 mg, 0.10 mmol), 4-*tert*-butylphenol (62 mg, 0.41 mmol), and anhydrous $K_2CO_3$ (55 mg, 0.40 mmol) were placed in a round-bottom flask. Subsequently, anhydrous NMP (20 mL) was added, and the reaction mixture was stirred at 85 °C for 5 h under an argon atmosphere. Afterward, toluene (50 mL) was added to the cooled reaction mixture, and the resultant solution was extracted with slightly acidic water (3 × 100 mL). The organic phase was collected, and toluene was removed by rotary evaporation. The crude product was purified by column chromatography on silica (2:1 $CH_2Cl_2$−hexane) to afford the desired product **9** (83 mg, 67%) as a purple solid. Mp 184−186 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.25 (s, 2H), 8.05 (s, 2H), 7.46 (t, $J$ = 8.0 Hz, 1H), 7.32 (d, $J$ = 8.8 Hz, 4H), 7.30 (d, $J$ = 8.0 Hz, 2H), 7.00 (d, $J$ = 8.8 Hz, 4H), 6.84−6.77 (m, 8H), 4.08−3.94 (m, 2H), 3.78 (s, 6H), 2.75−2.66 (m, 2H), 1.86−1.79 (m, 1H), 1.34−1.22 (m + singlet of *tert*-butyl groups, 26H), 1.09 (d, $J$ = 6.8 Hz, 12H), 0.90−0.82 ppm (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 163.41, 156.77, 156.65, 155.32, 153.19, 148.44, 147.34, 145.95, 133.12, 132.86, 131.11, 129.31, 126.71, 123.92, 122.81, 122.42, 121.33, 120.43, 119.41, 119.05, 118.91, 118.59, 114.82, 55.50, 44.03, 37.93, 34.25, 31.13, 30.70, 29.00, 28.69, 23.99, 23.65, 22.97, 13.81, 10.36 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{78}H_{78}N_2O_{10}$, 1202.5656; found, 1202.5699.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7,12-di-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (10).** This compound was prepared from compound **3** (0.25 g, 0.24 mmol), *p*-TsOH·$H_2O$ (0.14 g, 0.74 mmol), and *n*-heptane (21 mL) as per the procedure described for compound **7** to collect the product (0.21 g, 96%) as a dark red solid. Mp > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.72 (s, 2H), 8.25 (s, 2H), 7.49 (m, 5H), 7.33 (d, $J$ = 7.6 Hz, 2H), 7.15 (d, $J$ = 8.8 Hz, 4H), 2.74−2.66 (m, 2H), 1.37 (s, 18H), 1.15 ppm (d, $J$ = 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 162.57, 159.37, 156.67, 150.86, 149.20, 145.54, 135.48, 133.42, 132.84, 132.66, 130.10, 129.83, 129.57, 127.45, 124.42, 124.15, 121.91, 120.52, 120.05, 120.04, 119.77, 119.68, 34.63, 31.41, 29.23, 23.97 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{56}H_{47}Cl_2NO_7$, 915.2730; found, 915.2709.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-dichloro-7,12-di-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (11).** This compound was prepared from compound **10** (150 mg, 0.16 mmol), 2-ethyl-1-hexylamine (43 mg, 0.33 mmol), and toluene (10 mL) following the procedure described for compound **8**. The purification was performed on a silica-gel packed column (1:1 $CH_2Cl_2$−hexane) to obtain the desired product **11** (167 mg, 99%) as a dark red solid. Mp 212−214 °C (dec). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.70 (s, 2H), 8.27 (s, 2H), 7.50−7.42 (m, 5H), 7.33 (d, $J$ = 7.6 Hz, 2H), 7.16 (d, $J$ = 8.8 Hz, 4H), 4.11−4.00 (m, 2H), 2.75−2.66 (m, 2H), 1.92−1.82 (m, 1H), 1.48−1.24 (m + singlet of *tert*-butyl groups, 26H), 1.15 (d, $J$ = 6.8 Hz, 12H), 0.92−0.82 ppm (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 163.46, 162.73, 156.78, 151.14, 148.70, 145.58, 134.75, 133.36, 132.51, 132.44, 130.23, 129.75, 127.27, 124.50, 124.33, 124.11, 121.37, 119.79, 118.48, 118.36, 118.26, 44.59, 38.15, 34.58, 31.44, 30.82, 29.21, 28.82, 28.75, 24.08, 23.97, 23.06, 14.08, 10.62 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{64}H_{64}Cl_2N_2O_6$, 1026.4141; found, 1026.4166.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-di-(4-methoxyphenoxy)-7,12-di-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (12).** Weighed amounts of PBI **11** (100 mg, 0.10 mmol), 4-metoxyphenol (50 mg, 0.40 mmol), and anhydrous $K_2CO_3$ (55 mg, 0.40 mmol) were placed in an oven-dried round-bottom flask. Subsequently, anhydrous NMP (20 mL) was added, and the reaction mixture was stirred at 90 °C for 6 h under an argon atmosphere. Afterward, toluene (50 mL) was added to the cooled reaction mixture, and the resultant solution was washed with slightly acidic water (3 × 100 mL). The organic phase was collected, and toluene was removed by rotary evaporation. The crude product was purified by column chromatography on silica (2:1 $CH_2Cl_2$−hexane) to afford the desired product **12** (76 mg, 64%) as a purple solid. Mp 132−134 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.23 (s, 2H), 8.08 (s, 2H), 7.45 (t, $J$ = 8.0 Hz, 1H), 7.33 (d, $J$ = 8.4 Hz, 4H), 7.29 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 8.4 Hz, 4H), 6.84 (d, $J$ = 8.4 Hz, 4H), 6.79 (d, $J$ = 8.4 Hz, 4H), 4.10−3.98 (m, 2H), 3.76 (s, 6H), 2.71−2.63 (m, 2H), 1.90−1.82 (m, 1H), 1.38−1.24 (m + singlet of *tert*-butyl groups, 26H), 1.07 (d, $J$ = 6.8 Hz, 12H), 0.92−0.82 ppm (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 163.50, 163.35, 156.59, 156.40, 155.65, 153.25, 148.39, 147.35, 145.93, 132.98, 131.07, 129.28, 126.69, 123.91, 122.74, 122.45, 121.24, 120.64, 120.17, 120.12, 119.62, 118.98, 114.80, 55.47, 44.09, 37.95, 34.25, 31.14, 30.70, 28.97, 28.69, 23.99, 23.62, 22.98, 13.81, 10.37 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{78}H_{78}N_2O_{10}$, 1202.5656; found, 1202.5650.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-1,6-dichloro-7-(4-methoxyphenoxy)-12-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Monoimide Monoanhydride (13).** This compound was prepared by reaction of compound **6** (190 mg, 0.19 mmol), *p*-TsOH·$H_2O$ (108 mg, 0.57 mmol), and *n*-heptane (16 mL) following the procedure described for compound **7** to collect the product (154 mg, 93%) as a purple solid. Mp > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.74 (s, 1H), 8.72 (s, 1H), 8.24 (s, 1H), 8.15 (s, 1H), 7.51−7.45 (m, 3H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.18−7.12 (m, 4H), 7.00 (d, $J$ = 8.8 Hz, 2H), 3.87 (s, 3H), 2.74−2.66 (m, 2H), 1.37 (s, 9H), 1.15 ppm (d, $J$ = 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 162.61, 159.37, 159.33, 157.64, 157.20, 156.71, 150.86, 149.21, 146.53, 145.55, 135.48, 135.36, 133.50, 133.45, 132.87, 132.62, 130.09, 129.85, 129.76, 129.61, 127.46, 124.44, 124.17,



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121.88, 121.68, 120.42, 120.07, 120.01, 119.78, 119.62, 119.43, 119.29, 115.63, 55.73, 34.64, 31.42, 29.25, 23.98 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{53}H_{41}Cl_2NO_8$, 889.2276; found, 889.2269.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-dichloro-7-(4-methoxyphenoxy)-12-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (14).** Following the procedure described for compound **8**, this compound was prepared by reaction of compound **13** (150 mg, 0.17 mmol), 2-ethyl-1-hexylamine (44 mg, 0.34 mmol), and toluene (10 mL). The purification was performed on a column packed with silica gel (2:1 $CH_2Cl_2$–hexane) to obtain the desired product **14** (159 mg, 94%) as a purple solid. Mp > 250 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.72 (s, 1H), 8.70 (s, 1H), 8.26 (s, 1H), 8.16 (s, 1H), 7.51–7.45 (m, 3H), 7.33 (d, $J$ = 7.6 Hz, 2H), 7.18–7.13 (m, 4H), 6.98 (d, $J$ = 8.8 Hz, 2H), 4.12–4.02 (m, 2H), 3.86 (s, 3H), 2.75–2.66 (m, 2H), 1.90–1.84 (m, 1H), 1.40–1.24 (m + singlet of *tert*-butyl group, 17H), 1.15 (d, $J$ = 6.8 Hz, 12H), 0.92–0.84 ppm (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ = 163.46, 163.38, 162.75, 157.37, 156.83, 151.14, 148.71, 146.85, 145.58, 134.75, 134.61, 133.43, 133.38, 132.47, 130.26, 129.76, 127.27, 124.52, 124.34, 124.12, 121.74, 121.35, 119.80, 118.36, 118.30, 118.21, 117.84, 117.76, 115.49, 55.70, 44.56, 38.14, 34.58, 31.44, 30.82, 29.22, 28.81, 28.74, 24.06, 23.98, 23.06, 14.09, 10.62 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{61}H_{58}Cl_2N_2O_7$, 1000.3621; found, 1000.3608.

**Synthesis of *N*-(2,6-Diisopropylphenyl)-*N*′-(2-ethyl-1-hexyl)-1,6-di-(4-methoxycarbonylphenoxy)-7-(4-methoxyphenoxy)-12-(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxy Bisimide (15).** This compound was prepared as per the procedure described for compounds **9** and **12** by reaction of compound **14** (100 mg, 0.10 mmol), methyl 4-hydroxybenzoate (61 mg, 0.40 mmol), anhydrous $K_2CO_3$ (55 mg, 0.40 mmol), and anhydrous NMP (20 mL) at 90 °C for 24 h. After the workup, purification was performed on a column packed with silica gel using $CH_2Cl_2$ as the mobile phase to obtain the desired product **15** (75 mg, 61%) as a purple solid. Mp > 250 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.30 (s, 2H), 8.18 (s, 1H), 8.03 (s, 1H), 7.98 (d, $J$ = 7.2 Hz, 2H), 7.90 (d, $J$ = 7.2 Hz, 2H), 7.47 (t, $J$ = 7.2 Hz, 1H), 7.30 (d, $J$ = 7.6 Hz, 2H), 7.27 (d, $J$ = 7.2 Hz, 2H), 7.15 (d, $J$ = 7.2 Hz, 2H), 7.02 (d, $J$ = 7.6 Hz, 2H), 6.85–6.76 (m, 6H), 4.04–3.96 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 2.73–2.66 (m, 2H), 1.86–1.80 (m, 1H), 1.34–1.22 (m + singlet of *tert*-butyl group, 17H), 1.09 (d, $J$ = 6.8 Hz, 12H), 0.90–0.83 ppm (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 166.05, 165.99, 163.26, 163.07, 159.64, 159.57, 157.06, 156.84, 156.15, 154.14, 152.90, 148.28, 147.58, 145.93, 133.15, 132.65, 131.67, 131.50, 130.91, 129.40, 126.70, 126.03, 125.90, 123.98, 123.32, 123.29, 122.64, 122.29, 122.25, 121.58, 121.49, 121.35, 121.25, 119.83, 119.60, 119.26, 118.98, 118.92, 118.86, 115.04, 55.58, 51.83, 44.11, 37.93, 34.22, 31.06, 30.68, 29.04, 28.67, 23.97, 23.64, 22.96, 13.80, 10.33 ppm. MS (ESI-TOF): $[M]^+$ calculated for $C_{77}H_{72}N_2O_{13}$, 1232.5034; found, 1232.5076.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b01131.

Cyclic voltammograms of the all the compounds; structures of compounds PBI-$Cl_4$ and PBI-$(OPh)_4$; fluorescence decay curves of compounds **1**, **4**, **2**, **8**, **9** and relevant model compounds; structure elucidation of compounds **2**, **3**, **4**, **6**, **9**, **12**, and **15**; $^1$H and $^{13}$C NMR spectra of all synthesized compounds; and mass spectra of all the new compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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