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Di(alkoxy)- and Di(alkylthio)-Substituted Perylene-3,4;9,10-tetracarboxy Diimides with Tunable Electrochemical and Photophysical Properties

Chuntao Zhao, Yuexing Zhang, Renjie Li, Xiyou Li,* and Jianzhuang Jiang*

Department of Chemistry, Shandong University, Jinan 250100, China

xiyouli@sdu.edu.cn; jzjiang@sdu.edu.cn

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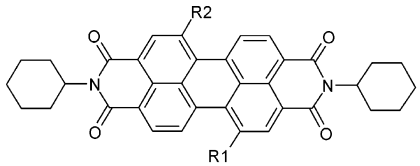

$R_1 = R_2 = OC_{12}H_{25}$, $SC_{12}H_{25}$, cyclohexylamine, thiophenyl;
$R_1 = OC_{12}H_{25}$, $R_2 = SC_{12}H_{25}$, cyclohexylamine, morpholine

Nucleophilic substitution of *N*,*N*′-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxydiimide (PTCDI) with an excess of corresponding alkanol in the presence of sodium hydride or anhydrous potassium carbonate at 85−100 °C provided both di(alkoxy)- and mono(alkoxy)-substituted PTCDI compounds, namely, *N*,*N*′-dicyclohexyl-1,7-di(alkoxy)perylene-3,4:9,10-tetracarboxydiimide (**3**) and *N*,*N*′-dicyclohexyl-1-bromo-7-alkoxyperylene-3,4:9,10-tetracarboxydiimide (**2**). Starting from mono(alkoxy)-substituted PTCDI, nucleophilic substitution with thiol, thiophenol, or alkylamine led to the formation of unsymmetrical 1,7-di(substituted) PTCDI compounds (**7**−**10**). For the purpose of comparative studies, symmetrical di(substituted) *N*,*N*′-dicyclohexyl-1,7-di(alkylthio)perylene-3,4:9,10-tetracarboxydiimide (**4**), *N*,*N*′-dicyclohexyl-1,7-di(thiophenyl)perylene-3,4:9,10-tetracarboxydiimide (**5**), and *N*,*N*′-dicyclohexyl-1,7-di(alkylamine)perylene-3,4:9,10-tetracarboxydiimide (**6**) have also been prepared by a similar nucleophilic substitution. These newly prepared PTCDI compounds have been characterized by a wide range of spectroscopic methods in addition to elemental analysis. Electronic absorption and fluorescence studies revealed that the absorption and emission bands as well as the fluorescence quantum yield can be tuned continuously over a large range by incorporating substituents with different electron-donating abilities.

Introduction

Perylene-3,4;9,10-tetracarboxydiimide (PTCDI) derivatives have attracted increasing attention in the past decade due to their potential applications in molecular electronics, such as field effect transistors,[1−8] solar cells,[9−14] light-harvesting arrays,[15−19] and light emitting diodes.[20−24] These functional dyes were also used in electrophotography[25] and lasers.[26,27] Furthermore, liquid crystal properties were recently demonstrated by PTCDI compounds as well as nano- and mesoscopic supramolecular structure.[28−33] These dyes have generated great interest because of their outstanding photochemical and thermal stability, ease of synthetic modification, and desirable optical and redox characteristics.

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Driven by their use in many different applications,[34] the structure of PTCDIs has been modified by introducing side groups either to the imide nitrogen atoms or at the bay positions (i.e., 1, 6, 7, 12 positions, Scheme 1). Incorporation of substituents to the imide nitrogen atoms has been found to increase the solubility of corresponding PTCDI derivatives in organic solvents and affect the packing model of PTCDI molecules in solid film.[35−37] However, substitution at the imide does not significantly affect the electronic structure and properties of PTCDI compounds because the nodes in both the HOMO and LUMO of PTCDI along the long axis of the molecule limit the electronic interactions between PTCDI and corresponding substituents.[2] In contrast, introduction of substituents at the bay positions of PTCDI was demonstrated to significantly alter the electronic properties, including electronic absorption spectra, fluorescence spectra, and redox potentials.[38−40] The substituents that have previously been incorporated onto the bay positions of PTCDIs are limited to phenoxy groups,[41−51] aryls,[38,43] cyclic secondary amines,[52−60] cyano groups,[1] and halogens.[61] To the best of our knowledge, there appears to be no report on PTCDI compounds with alkoxy and/or alkylthio substituents at their bay positions.

In the present work, we describe the synthesis and photophysical properties of a series of novel substituted PTCDIs with long alkoxy and/or alkylthio groups at the bay positions of the PTCDI ring. As opposed to bulky phenoxy or cyclic secondary amines, the long linear alkoxy and/or alkylthio groups cause less of a perturbation to the planar conformation of PTCDI core due to their smaller steric hindrance. This, in addition to the hydrophobic interaction between long alkyl chains[62−64] and strong electron-donating nature of long alkoxy groups, induces novel photophysical properties to PTCDIs.

Results and Discussion

Synthesis. Nucleophilic substitution of halogens on the PTCDI ring has been employed to prepare phenoxy- and secondary cycloamino-substituted PTCDI compounds.[47,51,52,55,59] However, there has been no report on the long alkoxy-substituted

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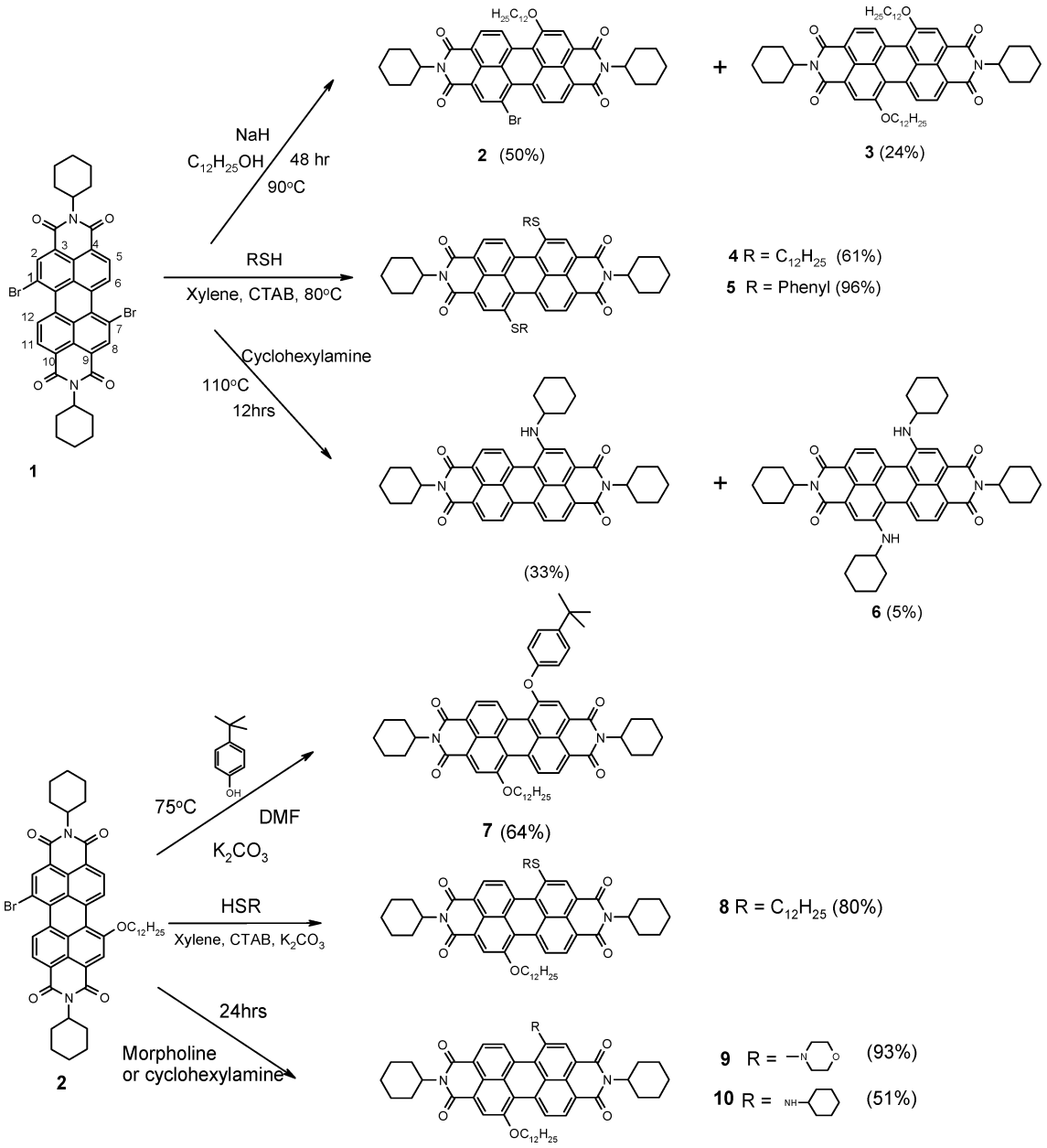
SCHEME 1. Synthesis of Compounds 3−10



PTCDI derivatives prepared by this methodology, probably due to the weaker nucleophilicity of alkanols compared to that of phenols. Trials of the reaction between halogenated PTCDIs, for example, **1**, and alkanol in polar organic solvents such as DMF, NMP, and DMSO, which was used to prepare the phenoxy-substituted PTCDIs, failed to provide the target long alkoxy-substituted PTCDI compounds. Both the target mono- and di(alkoxy)-substituted PTCDI compounds were, however, obtained from the reaction between halogenated PTCDIs and excess alkanol with sodium hydride or anhydrous potassium carbonate as a promoter at 85−100 °C (Scheme 1). Reaction temperature in this range proved to be crucial for the good reaction yields, as a lower or higher reaction temperature led to lower production yield of the corresponding long alkoxy-substituted PTCDI compounds. It is worth pointing out that the yield of disubstituted product **3** is always lower than that of monosubstituted **2**, no matter what kind of reaction conditions were adopted. It is also noteworthy that we carried out a two-phase reaction procedure with toluene or xylene and water as solvents, potassium hydroxide or anhydrous potassium carbonate as the base, and cetyltrimethylammonium bromide (CTAB) or 18-crown-6 as phase transfer catalyst, which, however, led to the isolation of alkoxy-substituted PTCDI compounds in very low yield.

As expected, the mono(alkoxy)-substituted **2** with one remaining halogen atom in the PTCDI ring can react further with a phenol or secondary cyclic amine, such as 4-*tert*-butylphenol and morpholine, respectively, under reported reaction conditions to form unsymmetrical 1-(alkoxy)-7-(phenoxy)- or 1-(alkoxy)-7-(morpholinyl)-substituted PTCDI compounds, **9** and **10**, with good reaction yield. These appear to represent the first example of PTCDI compounds with two different electron-donating groups at bay positions of the PTCDI ring.

Alkylthio-substituted PTCDI compounds can also be provided with the newly developed reaction route starting from halogenated PTCDI compound **1** and excess of alkylthiols. Due to

TABLE 1. Photophysical Properties of Molecules 3−12

compound	λ_{abs} (nm)	ϵ ($mol^{-1}\cdot L\cdot cm^{-1}$)	λ_{em} (nm)	Φ_f (%)	τ (ns)
3	570	5.41×10^4	597	72.4	5.4
4	574	3.16×10^4	655	15.5	8.5
5	556	3.51×10^4	651	18.6	7.8
6	703	3.17×10^4	761	0.8	1.4
7	558	5.14×10^4	588	82.7	5.0
8	568	4.12×10^4	640	39.0	7.8
9	606	3.49×10^4	697	6.7	3.4
10	640	3.26×10^4	722	1.0	0.8
11	546	4.13×10^4	578	96.2	4.5
12	526		534	100	3.8

the stronger nucleophilicity of alkylthio groups than that of alkoxy groups, reaction between **1** and alkylthiols occurs much more easily and gives di(alkylthio)-substituted PTCDI compound **4** instead of the mono(alkylthio)-substituted PTCDI compound as the main product. As also displayed in Scheme 1, this reaction happened in a phase transfer system with xylene as organic solvent, potassium carbonate as the base, CTAB as a PT catalyst, and even without utilization of any aqueous phase. With the mono(alkoxy)-substituted **2** as starting material, similar reaction with alkylthiol led to the isolation of unsymmetrical substituted PTCDI compound **8** in high yield.

For the substitution with thiophenol, reaction with halogenated PTCDI **1** was found to take place under more milder reaction conditions, without utilization of any phase transfer reagent and providing di(phenylthio)-substituted PTCDI compound **5** in high yield, because of the extremely increased nucleophilicity of the thiophenyl group.

The reaction of halogenated PTCDIs with alkylamines has been the focus of several literature reports. As mentioned above, secondary cyclic amines, such as piperidine, morpholine, and pyrrolidine, have been introduced onto the PTCDI rings to form di(amino)−PTCDI compounds by the reaction of halogenated PTCDIs with an excess of corresponding cyclic secondary amines according to Wasielewski and co-workers.[52] However, to the best of our knowledge, introduction of two primary alkylamino groups onto the PTCDI ring seems limited to an octylamino group.[65] Reactions of halogenated PTCDI compound **1** with a primary alkylamine, such as cyclohexylamine, led to the formation of corresponding di(cyclohexylamino)−PTCDI compound **6** in low reaction yield in addition to the mono-(cyclohexylamino)−PTCDI compound as the main product. In line with previous findings,[65] the debrominated product was isolated as the side product of this reaction.

In addition, efforts to connect the secondary alkoxy or secondary noncyclic alkylamino groups onto the PTCDI rings have also been conducted. However, the reaction of cholesterol, cyclohexanol, 2-ethylhexane-2-ol, or diethylamine with halogenated PTCDI compound **1** failed to give any nucleophilic mono- or disubstituted product, indicating that the steric hindrance might dominate this reaction process.

Satisfactory elemental analysis results were obtained for all the newly prepared PTCDI compounds **3**−**10**. The compounds were further characterized by MALDI-TOF and ^{1}H NMR. The asymmetrical substitution pattern of compounds **7**−**10** was supported by the splitting signals of the aromatic PTCDI protons in their ^{1}H NMR spectra.

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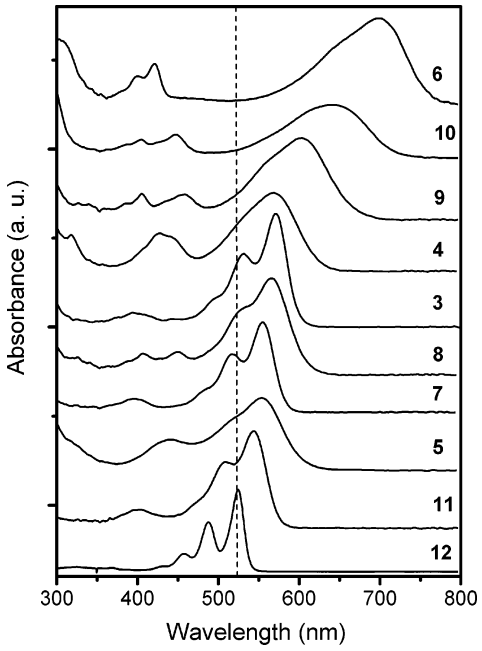

FIGURE 1. UV−vis absorption spectra of compounds **3**−**12** in chloroform.

UV−Vis Absorption. The electronic absorption spectra of compounds **3**−**10** were recorded in $CHCl_3$, and the data are summarized in Table 1. Figure 1 displays the UV−vis absorption spectra for compounds **3**−**10** together with that of two model compounds, namely, *N*,*N*′-dicyclohexyl-1,7-bi(4-*tert*-butyl)phenoxy)perylene-3,4:9,10-tetracarboxy diimide (**11**) and *N*,*N*′-dicyclohexyl)perylene-3,4:9,10-tetracarboxydiimide (**12**). All of these compounds show intense absorption in the UV−vis region with a large extinction coefficient. Compared with the parent PTCDI **12**, the main absorption bands of **3**−**11** become broadened and gradually shift to the red side depending on the identity of substitution groups on the PTCDI ring.

The maximum absorption peak of parent PTCDI **12** is at 525 nm, while that of compound **11** is shifted to 546 nm due to the introduction of two electron-donating phenoxy groups onto the PTCDI ring.[66,67] Incorporation of two alkoxy groups as opposed to phenoxy groups in compound **3** further red shifts the main absorption band to 570 nm. Just as expected, the asymmetrical disubstituted PTCDI compound **7** with one phenoxy group and one alkoxy group at the bay positions of the PTCDI ring shows a red-shifted absorption band at 558 nm, just between those of compound **11** with two phenoxy groups and compound **3** with two alkoxy groups.

Similar to the introduction of alkoxy and phenoxy groups onto the PTCDI ring, incorporation of two alkylthio and thiophenyl groups, also with electron-donating properties, leads to the red shift of the main absorption band to 574 and 556 nm for compounds **4** and **5**, respectively (Table 1).

As revealed in Table 1, the largest red shift in the main absorption band was observed for the alkylamino-substituted PTCDI compounds including **6**, **9**, and **10**. This effect is probably associated with increased electron-donating properties

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TABLE 2. Calculated HOMO and LUMO Energy of Compounds 1−10 by AM1

compound	HOMO (eV)	LUMO (eV)	twisting angle (°)
3	−8.465	−2.227	9.0
4	−8.472	−2.482	21.5
5	−8.351	−2.526	21.7
6	−7.947	−2.050	27.8
7	−8.551	−2.297	18.0, 18.3[a]
8	−8.527	−2.402	18.2, 21.4[a]
9	−8.406	−2.209	18.6, 24.4[a]
10	−8.112	−2.122	18.4, 25.1[a]
11	−8.810	−2.436	18.5
12	−8.826	−2.454	0

[a] Two twisting angles for one molecule because of the different substitutions at the 1,7 position.

of alkylamino groups. Introduction of one cyclohexylamino group onto the PTCDI ring red shifts the main absorption band of compound **10** to 640 nm, whereas introduction of the second cyclohexylamino group shifts it further to 703 nm in compound **6**. Nevertheless, comparison of the main absorption band between the two mono(alkylamino)-substituted PTCDI compounds, 640 nm for **10** with one primary alkylamino group on the PTCDI ring, 606 nm for **9** with one secondary alkylamino group, clearly indicates different tuning ability to the main absorption band of PTCDI derivatives between the primary and secondary alkylamino groups.

On the basis of previous reports,[2,38,46,57,68] the broadening and loss of detailed vibronic structure for the absorption bands of PTCDI compounds **4**, **5**, **6**, **8**, **9**, and **10** were attributed to both the participation of the side groups in the conjugation of the PTCDI core and the twisting in molecular conformation of the PTCDI ring because of the 1,7 disubstitution. According to our calculation results using the AM1 method (Table 2), the bigger twisting angle obtained for compound **4** in comparison with **3** is in line with the experimentally observed more significant broadening in the main absorption bands of compound **4** than that in **3**. A similar degree of broadening was observed for the main absorption bands of compounds **6**, **9**, and **10** to that of **4**, corresponding well with the similar twisting angle obtained by calculations for all of these compounds. Furthermore, significantly different broadening of the main absorption bands observed for compounds **5** and **11** with similar twisting angle, 21.7 and 18.5° for **5** and **11**, respectively, is attributed to different participation extent in the conjugation of the PTCDI core between the thiophenyl and phenyloxy side groups. This argument is also supported by the orbital analysis described below.

As summarized in Figure 1, successful tuning of the electronic absorption spectra over a large range (400−800 nm) has been realized by introducing different electron-donating substituents, including alkoxy, alkythio, phenoxy, thiophenyl, and alkylamino groups to the bay positions of the PTCDI ring.

Fluorescence. The fluorescence spectra of compounds **3**−**11** are recorded in chloroform with excitation at 410 nm. Fluorescence quantum yields (Φ_f) are calculated with parent compound PTCDI **12** as the standard.[38] Figure 2 displays the fluorescence spectra of these compounds, and Table 1 summarizes the experiment data.

In line with the red-shifted electronic absorption bands, the emission band of all substituted PTCDI compounds also shifts

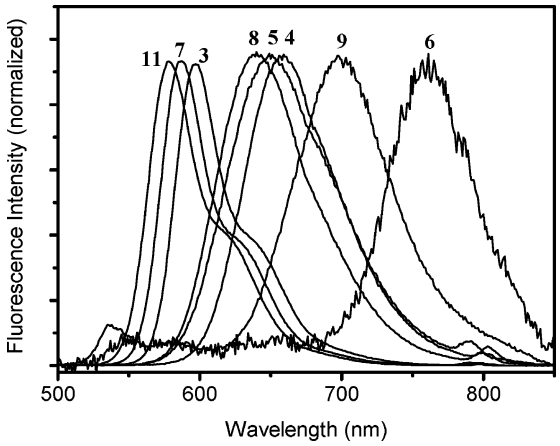

FIGURE 2. The normalized fluorescence spectra of compound **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **11** in chloroform with excitation at 410 nm.

to the red, following the same order observed for corresponding main absorption bands, due to the incorporation of various kinds of electron-donating substituents at the bay position(s) of the PTCDI ring (Figure 2). Additionally, the alkylthio- and thiophenyl-substituted PTCDI compounds **4**, **5**, and **8** were found to display larger Stokes shift in comparison with that of alkoxy- and phenoxy-substituted analogues **3** and **11**, indicating larger structure relaxation during the photoexcitation process.

Due to the very strong electron-withdrawing nature of the PTCDI core, introducing electron-donating side groups onto the bay positions of the PTCDI core leads to charge transfer character in the excited state of the PTCDI molecules, which in turn results in a significant decrease in the fluorescence quantum yield (Table 1). This corresponds well with the result found for other PTCDI compound systems.[38,65]

The fluorescence lifetimes measured by the phase modulation method for all of these PTCDI compounds are summarized in Table 1, which also shows dependence on the number and, in particular, identity of substituents on the bay positions of the PTCDI core. For example, the fluorescence lifetime recorded for di(alkoxy)-substituted PTCDI **3**, 5.4 ns, is longer than that for di(phenoxy)-substituted PTCDI **11**, 4.5 ns, because of the more stable excited state of the former.[69] However, the longest fluorescence lifetime was actually observed for the alkylthio- and thiophenyl-substituted PTCDI compounds **4**, **5**, and **8**, indicating the most stable excited state of these compounds. In contrast, the alkylamino-substituted compounds of **6**, **9**, and **10** showed the shortest fluorescence lifetime among the PTCDI derivatives of **3**−**12** due to the electron transfer between the PTCDI core and alkylamino side groups. These experimental results will be rationalized on the basis of AM1 calculations and orbital analysis below.

Electrochemical Properties. The electrochemical behavior of all the disubstituted PTCDI compounds was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. The half-wave redox potential values versus SCE for all the disubstituted compounds (**3**−**10**) together with two model compounds, **11** and **12**, are summarized in Table 3. Figure 3 shows the cyclic voltammograms and differential pulse voltammograms of unsymmetrical disubstituted PTCDI **8** as a

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(69) Sinks, L. E.; Rybtchinski, B.; Iimura, M.; Jones, B. A.; Goshe, A. J.; Zuo, X.; Tiede, D. M.; Li, X.; Wasielewski, M. R. *Chem. Mater.* **2005**, *17*, 6295−6303.

(70) Langhals, H.; Jona, W. *Eur. J. Org. Chem.* **1998**, 847−851.

TABLE 3. Half-Wave Redox Potentials[a] (vs SCE) of 3−12 in CH_2Cl_2

compound	Oxd_2	Oxd_1	Red_1	Red_2	$E^o_{1/2}$[b]
3	1.79	1.31	−0.76	−0.92	2.07
4	1.79	1.37	−0.62	−0.83	1.99
5	1.45	1.45	−0.55	−0.76	2.00
6	0.84	0.72	−0.82	−1.01	1.54
7	1.59	1.38	−0.70	−0.89	2.08
8	1.83	1.33	−0.68	−0.87	2.01
9	1.24	1.03	−0.71	−0.90	1.74
10	1.39	0.91	−0.78	−0.96	1.69
11		1.44	−0.85	−0.67	2.29
12		1.62	−0.58	−0.81	2.20

[a] Values obtained by DPV in dry CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte and Fc/Fc^+ as internal standard. [b] $E^o_{1/2} = Oxd_1 - Red_1$.

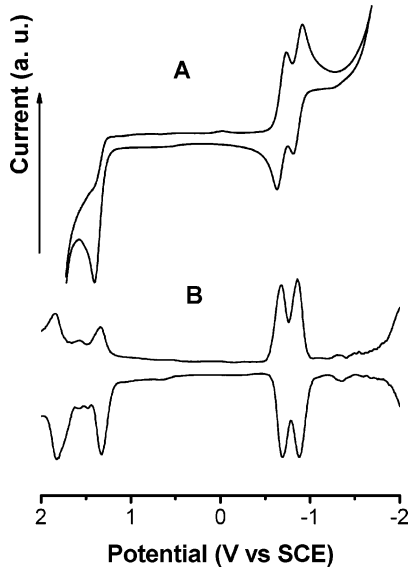

FIGURE 3. CV (A) and DPV (B) plot of compound **8** in dichloromethane containing 0.1 M TBAP.

representative of the series of compounds. Within the electrochemical window of CH_2Cl_2, all the disubstituted PTCDI compounds undergo two quasi-reversible one-electron oxidations and two quasi-reversible one-electron reductions as the separation of the reduction and oxidation peak potentials for each process is 60−95 mV. All these processes are attributed to successive removal from or addition of electron to the PTCDI orbitals. The oxidations and reductions are labeled as Oxd_n and Red_n, respectively.

The effect of substituent species and substitution number is clearly reflected by the shift in the half-wave potentials of the first oxidation and first reduction of compounds **3**−**10**. As can be seen in Table 3, substitution of two alkoxy groups at the bay positions of compound **3** induces significant shift to the *negative* direction for both the first oxidation and first reduction, relative to parent PTCDI **12**, reflecting the electron-donating nature of alkoxy groups attached onto the bay positions of the PTCDI ring. Replacement of one alkoxy group in compound **3** with one phenoxy group in **7** results in shift to the *positive* direction of the first oxidation as well as the first reduction processes, suggesting the larger electron-donating ability of the alkoxy group in comparison with that of phenoxy group.

The effect of alkylthio and thiophenyl groups at bay positions of the PTCDI core on their electrochemistry is clearly revealed by the experimental results of compounds **4** and **5** organized in Table 3. Incorporating two alkylthio groups at the bay positions of PTCDI in compound **4** induces a great shift to the *negative* direction of the first oxidation potential and slight shift to the *negative* direction of the first reduction potential, relative to parent PTCDI **12**, again reflecting the same electron-donating nature of the alkythio group. However, the relatively slight shift for both the first oxidation and first reduction potential in compound **4** induced by two alkylthio groups as opposed to that in **3** by two alkoxy groups suggests relatively weaker electron-donating properties of the alkylthio group than that of the alkoxy group. As can be expected, the shift to the *negative* direction of both the first oxidation and first reduction potentials of unsymmetrical PTCDI compound **8** locates the potentials between those of the symmetrical disubstituted counterparts **3** and **4** (Table 3). Examination of electrochemical data in Table 3 also reveals that introducing two thiophenyl groups onto the bay positions of the PTCDI ring leads to a significant shift to the *negative* direction of the first oxidation potential but a slight shift to the *positive* direction of the first reduction potential, therefore reducing the potential difference between these two redox processes.

At the end of this section, it is worth pointing out that the stronger electron-donating property of the alkylamino groups in comparison with that of either alkoxy, phenoxy, or alkylthio substituents is clearly revealed by the larger shift to the *negative* direction of the first oxidation and first reduction potentials for the mono- and di(alkylamino)-substituted PTCDI compounds **6**, **9**, and **10** than that for di(alkoxy)-, di(phenoxy)-, and di(alkylthio)-substituted analogues **3**, **4**, **7**, and **8** (Table 3).

AM1 Calculation. To enhance our understanding of the effect of substituents on the electronic spectra and electrochemistry of PTCDI compounds, we carried out molecular orbital (MO) calculations on compounds **3**−**12** at the AM1 level. The calculated molecular orbital (HOMO and LUMO) energies are summarized in Table 2. Most of the trends found by experimental measurements in the potentials of the first oxidation and first reduction processes and, in particular, the decrease in the HOMO−LUMO gap, according to different types of the substituents on the PTCDI ring, are reproduced by calculation.

According to the calculation results, incorporation of alkoxy and phenoxy groups onto the bay positions of the PTCDI core increases the energy level of both HOMO and LUMO and slightly reduces the energy gap between the HOMO and LUMO (Table 2). This not only corresponds well with the electrochemical measurement results but also is in line with the red shift of the main absorption band observed in the UV−vis spectrum of compounds **3**, **7**, and **11** in comparison with that of the parent PTCDI **12**.

Calculation on the molecular orbital energies for alkythio- and thiophenyl-substituted compounds **4**, **5**, and **8** reveals that incorporating two alkylthio or thiophenyl groups onto the bay positions of the PTCDI ring induces a significant positive shift in the energy level of the HOMO while the energy level of LUMO remained almost unchanged, leading to a decrease in the HOMO−LUMO gap, compared with those of parent PTCDI compound **12**. As clearly shown in Figure 4, the HOMO of compound **4** locates on the sulfur atoms and the carbon atoms which close to the sulfur on the PTCDI core, while the LUMO is only PTCDI core centered. This dichotomy explains how introduction of alkylthio groups onto the PTCDI ring significantly affects the energy level of HOMO but has no effect on

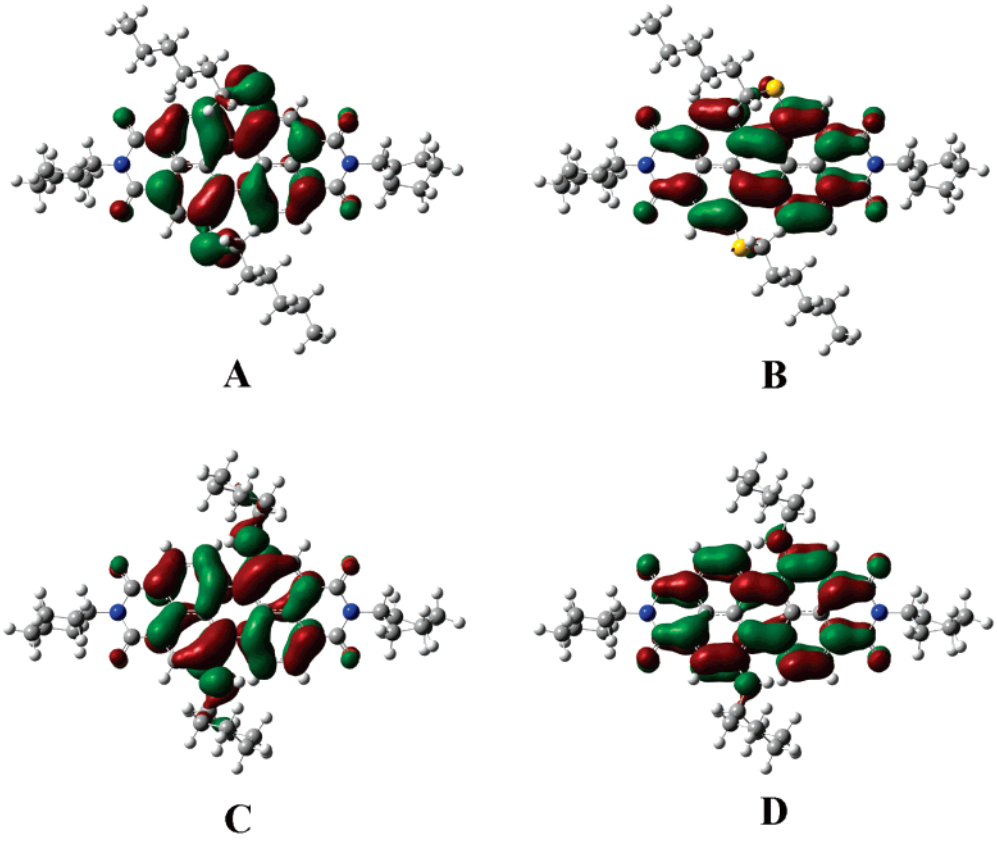

FIGURE 4. Calculated molecular orbitals of **4** and **6**: (A) HOMO of **4**; (B) LUMO of **4**; (C) HOMO of **6**; (D) LUMO of **6**.

that of LUMO. These results also agree well with the experimental findings as described above.

With excitation of compound **4** from ground state to the first excited state, electron transfer takes place from the HOMO (on the alkylthio groups) to the LUMO (on the PTCDI core), resulting in the charge transfer nature for the excited state of this compound. This induces significant change on the distribution of electronic density over the whole molecule and thus a large structure relaxation, which is then responsible for the observation of the broadened absorption band in the UV−vis spectrum and a big Stokes shift for compound **4** as well as analogous **5** and **8**. The decay of the excited state of this compound (charge recombination) is also accompanied by the redistribution of the electron density and a large structure relaxation and therefore needs a large amount of activation energy. As a consequence, the decay rate of the excited sate for this compound is decreased and the fluorescence lifetime prolonged.

As tabulated in Table 2, more significant increase in the energy level of both HOMO and LUMO and decrease in the HOMO−LUMO gap have been revealed for the PTCDI compounds **6**, **9**, and **10** with the introduction of mono- or di-(alkylamino) substituents onto the PTCDI ring, according to the calculations. These accurately produce the experimental results that introduction of the alkylamino groups onto the bay positions of the PTCDI ring induces the largest shift to the *negative* direction of the first oxidation and first reduction potentials and the largest red shift in the main absorption band for these compounds in comparison with those substituted by alkoxy, alkylthio, phenyloxy, and thiophenyl groups. Calculations also indicate that both the HOMO and LUMO of compound **6** are centered on the PTCDI core, with the HOMO extended to the amino side groups (Figure 4). The contribution from the amino side groups to the HOMO results in partial charge separation for the ground state and excited state and is responsible for both the low fluorescence quantum yield and the short fluorescence lifetime of compound **6**. This is also true for the analogues **9** and **10**.[38]

Conclusion

A series of novel symmetrical and unsymmetrical disubstituted PTCDI compounds with alkoxy, alkylthio, and/or thiophenyl groups at the bay positions of the PTCDI ring have been prepared by nucleophilic substitution. Successful tuning of the electronic absorption spectra and fluorescence spectra over a large range has been realized by introducing a different number of substituents with varying electron-donating ability onto the bay positions of the PTCDI ring.

Experimental Section

(*N*,*N*′-Dicyclohexyl-1,7-dibromo)perylene-3,4:9,10-tetracarboxydiimide (**1**),[65] **11**,[47] and **12**[70] were prepared following the literature methods. All other chemicals were purchased from commercial source. Solvents were of analytical grades and were purified by the standard method.

(*N*,*N*′-Dicyclohexyl-1,7-didodecyloxy)perylene-3,4;9,10-tetracarboxydiimide (3) and (*N*,*N*′-Dicyclohexyl-1-bromo-7-dodecyl)-perylene-3,4;9,10-tetracarboxydiimide (2). A mixture of dodecanol (15 mL) and sodium hydride (60 mg, 2.5 mmol) was stirred at room temperature for 15 min. Then **1** (320 mg, 0.45 mmol) was added to the reaction mixture. The mixture was heated to 90 °C

and kept at this temperature for 24 h. Methanol (60 mL) was added to the reaction mixture after it was cooled to room temperature. The purple precipitate was isolated from the reaction mixture by filtration and was washed with methanol thoroughly three times. The crude product was chromatographed on silica gel with chloroform as eluent. The first fraction contains **3** (72 mg, yield 17%): mp >280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 7.92 (s, 2H), 4.98 (m, 2H), 4.22 (m, 4H), 2.59 (m, 4H), 1.99 (m, 8H), 1.91 (m, 4H), 1.49−1.25 (br, 44H), 0.89 (t, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.2, 162.8, 155.9, 132.5, 127.7, 127.6. 127.4, 122.6, 122.3, 120.8, 119.2, 115.6, 69.8, 69.7, 53.7, 53.5, 53.3, 31.4, 29.2, 29.1, 29.0, 28.9, 28.6, 26.2, 26.0, 25.1, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 923.7, calcd for $C_{60}H_{78}N_2O_6$ (*m*/*z*), 923.3. Anal. Calcd for $C_{60}H_{78}N_2O_6$: C, 78.05; H, 8.52; N, 3.03. Found: C, 77.67; H, 8.55; N, 2.98.

From the second red fraction, (*N*,*N*′-dicyclohexyl-1-bromo-7-dodecyloxy)perylene-3,4;9,10-tetracarboxydiimide (**2**) was collected (161 mg, yield 44%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (d, J = 7.84 Hz, 1H), 9.08 (d, J = 7.79 Hz, 1H), 8.56 (s, 1H), 8.35 (d, J = 7.84 Hz, 1H), 8.29 (d, J = 7.79 Hz, 1H), 8.18 (s, 1H), 5.00 (m, 2H), 4.32 (m, 2H), 2.56 (m, 2H), 1.95 (m, 8H), 1.93 (m, 8H), 1.49−1.25 (br, 22H), 0.87 (t, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.0, 163.0, 162.9, 162.3, 156.8, 137.2, 132.8, 312.6, 131.7, 130.3, 128.5, 128.3, 127.8, 127.5, 126.9, 126.6, 124.0, 122.9, 112.5, 122.0, 121.2, 119.1, 118.7, 117.1, 70.1, 53.7, 53.6, 31.4, 29.2, 29.1, 29.1, 28.8, 28.8, 28.7, 28.6, 26.1, 25.8, 25.0, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 817.3, calcd for $C_{48}H_{53}BrN_2O_5$, *m*/*z* 817.9. Anal. Calcd for $C_{48}H_{53}BrN_2O_5$: C, 70.49; H, 6.53; N, 3.43. Found: C, 70.63; H, 6.37; N, 3.31.

(*N*,*N*′-Dicyclohexyl-1,7-di(dodecylthio))perylene-3,4;9,10-tetracarboxydiimide (4). A mixture of **1** (80 mg, 0.11 mmol), xylene (10 mL), potassium carbonate anhydrous (162 mg), water (2.0 mL), CTAB (10 mg), and 1-dodecylthiol (60 mg, 0.3 mmol) was heated to 85 °C under nitrogen. The reaction mixture was kept at this temperature for about 2 h, and then the solvents were evaporated under reduced pressure. The residue was column chromatographed on silica gel with chloroform as eluent. The second red fraction was collected. After recrystallization from chloroform and methanol, **4** was collected as red solid (140 mg, yield 61%): mp 93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, J = 10.4 Hz, 2H), 8.66 (s, 2H), 8.58 (d, J = 10.4 Hz, 2H), 5.00 (m, 2H), 3.15 (t, 4H), 2.57 (q, 4H), 1.95 (m, 4H), 1.80 (m, 4H), 1.55 (m, 4H), 1.50−1.21 (br, 44H), 0.86 (t, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.3, 163.2, 137.9, 131.8, 131.6, 130.1, 128.2, 128.2, 127.7, 124.8, 121.9, 121.4, 53.6, 35.4, 31.4, 29.2, 29.0, 29.0, 28.9, 28.8, 28.7, 28.6, 28.4, 27.9, 26.1, 25.0, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 955.3, calcd for $C_{60}H_{78}N_2O_4S_2$ (*m*/*z*), 955.4. Anal. Calcd for $C_{60}H_{78}N_2O_4S_2$: C, 75.43; H, 8.23; N, 2.93. Found: C, 75.56; H, 8.31; N, 2.87.

(*N*,*N*′-Dicyclohexyl-1,7-di(thiophenyl))perylene-3,4;9,10-tetracarboxydiimide (5). Following the similar procedures of **4** except using thiophenol instead of dodecylthiol, we got **5** as red solid (yield 94%): mp >280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, 2H), 8.50 (d, 2H), 8.48 (s, 2H), 7.43 (m, 10H), 4.97 (t, 2H), 2.54 (q, 4H), 1.90 (d, 4H), 1.72 (d, 6H), 1.44−1.28 (br, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.1, 162.8, 137.9, 133.6, 132.7, 132.5, 131.7, 131.3, 129.9, 129.2, 128.5, 128.4, 127.5, 125.2, 122.2, 121.7, 53.5, 28.6, 26.1, 24.9; MALDI-TOF MS (*m*/*z*) 769.0, calcd for $C_{48}H_{38}N_2O_4S_2$ (*m*/*z*), 770.0. Anal. Calcd for $C_{48}H_{38}N_2O_4S_2$: C, 74.78; H, 4.97; N, 3.61. Found: C, 74.53; H, 4.82; N, 3.68.

(*N*,*N*′-Dicyclohexyl-1,7-di(cyclohexylamino))perylene-3,4;9,-10-tetracarboxydiimide (6). 1 (260 mg, 0.32 mmol) was added to cyclohexylamine (15 mL). The reaction mixture was heated to 110 °C under nitrogen and then kept at this temperature for 12 h. The reaction mixture was cooled to room temperature, and the solvents were evaporated under reduced pressure. The deep green residue was column chromatographed on silica gel with chloroform as eluent. The second green band was collected, and **6** was collected as deep green solid (18 mg, 5%): mp >280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 10.8 Hz, 2H), 8.01 (d, J = 10.8 Hz, 2H), 7.83 (s, 2H), 5.81 (d, 2H), 5.04 (m, 2H), 3.45 (br, 2H), 2.58 (m, 4H), 2.05 (m, 4H), 1.92 (m, 4H), 1.56−1.26 (m, 24H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.7, 163.1, 144.0, 133.4, 129.7, 126.2, 122.3, 121.6, 120.2, 119.7, 115.9, 112.7, 53.5, 51.7, 32.6, 28.6, 26.1, 25.1, 25.0, 24.3; MALDI-TOF MS (*m*/*z*) 748.4, calcd for $C_{48}H_{52}N_4O_4$ (*m*/*z*), 748.9. Anal. Calcd for $C_{48}H_{52}N_4O_4(CHCl_3)_{0.25}$: C, 74.33; H, 6.68; N, 7.19. Found: C, 74.38; H, 6.98; N, 7.01.

(*N*,*N*′-Dicyclohexyl-1-dodecyloxy-7-(4-*tert*-butylphenoxy))perylene-3,4;9,10-tetracarboxydiimide (7). 2 (81 mg, 0.1 mmol) was mixed with potassium carbonate anhydrous (60 mg), 4-*tert*-butylphenol (25 mg, 0.16 mmol), and dried DMF (10 mL). The mixture was heated to 70 °C under the protection of nitrogen and was stirred at this temperature for about 2 h. The reaction mixture was cooled to room temperature and acidified with HCl (15 mL, 2 M L^{-1}). The red solid was separated by filtration and washed with water and methanol. The crude material was purified via flash column chromatography on silica gel using chloroform as eluent to give **7** as red solid (57 mg, yield 64%): mp >232 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (d, J = 8.8 Hz, 1H), 9.18 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.8 Hz, 1H), 8.07 (s, 1H), 8.02 (s, 1H), 7.45 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 5.01 (m, 2H), 4.49 (m, 2H), 2.55 (m, 4H), 2.08 (m, 2H), 1.92 (m, 4H), 1.77 (m, 4H), 1.55−1.27 (m, 32H), 0.88 (t, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.1, 163.0, 162.9, 162.6, 156.1, 154.3, 151.9, 147.5, 133.1, 131.9, 128.8, 128.2, 127.8, 127.7, 126.9, 123.2, 123.1, 122.4, 121.7, 121.2, 118.6, 116.4, 70.0, 53.6, 53.5, 53.3, 34.0, 31.4, 31.0, 29.2, 29.1, 29.0, 28.9, 28.6, 26.1, 25.9, 25.1, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 887.0, calcd for $C_{58}H_{66}N_2O_6$ (*m*/*z*), 887.2. Anal. Calcd for $C_{58}H_{66}N_2O_6$: C, 78.52; H, 7.50; N, 3.16. Found: C, 78.32; H, 7.37; N, 3.14.

(*N*,*N*′-Di(cyclohexyl)-1-dodecyloxy-7-dodecylthio)perylene-3,4;9,10-tetracarboxydiimide (8). 2 (120 mg, 0.15 mmol) was mixed with CTAB (6 mg, 0.01 mmol), potassium carbonate anhydrous (0.16 g), *o*-xylene (8 mL), and dodecylthiol (40 mg, 0.2 mmol) and heated to 80 °C. The mixture was stirred at this temperature for 5 h, and then the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with chloroform as eluent to get the product **8** as a red solid (110 mg, yield 80%): mp 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (m, 1H), 8.56 (m, 2H), 8.49 (s+d, 2H), 8.30 (s, 1H), 5.06 (m, 2H), 4.47 (m, 2H), 3.14 (m, 2H), 2.59 (m, 4H), 2.06(m, 2H), 1.96 (m, 4H), 1.82 (m, 4H), 1.63−1.20 (m, 46H), 0.87 (m, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.3, 163.3, 163.3, 163.3, 156.5, 137.1, 132.4, 130.3, 129.0, 128.8, 128.3, 127.5, 127.2, 125.0, 123.4, 122.5, 122.0, 121.2, 121.1, 119.7, 116.6, 70.0, 53.6, 53.5, 35.9, 31.4, 31.4, 29.2, 29.2, 29.1, 29.1, 29.0, 29.0, 28.9, 28.8, 28.7, 28.6, 26.1, 25.0, 22.2, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 938.2, calcd for $C_{60}H_{78}N_2O_5S$ (*m*/*z*), 939.4. Anal. Calcd for $C_{60}H_{78}N_2O_5S$: C, 76.72; H, 8.37; N, 2.98. Found: C, 76.99; H, 8.53; N, 2.84.

(*N*,*N*′-Dicyclohexyl-1-dodecyloxy-7-morpholinyl)perylene-3,4;9,10-tetracarboxydiimide (9). The mixture of **2** (128 mg, 0.16 mmol) and morpholine (12 mL) was heated to 85 °C and stirred at this temperature for 24 h. Then the solvents were evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane as eluent to get product **9** as a deep green solid (121 mg, yield 93%): mp 154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (d, J = 8.2 Hz, 1H), 9.32 (d, J = 8.1 Hz, 1H), 8.45 (d+d, 2H), 8.40 (s, 1H), 8.32 (s, 1H), 5.06 (m, 2H), 4.41 (t, 2H), 3.92 (m, 4H), 3.29 (d, 2H), 3.03 (m, 2H), 2.60 (q, 4H), 2.06−1.28 (m, 36H), 0.90 (t, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.5, 163.4, 163.2, 163.1, 156.1, 149.6, 133.9, 133.1, 129.1, 128.5, 128.4, 127.6, 124.1, 124.0, 123.0, 122.9, 122.3, 121.3, 121.2, 120.4, 117.1, 69.9, 66.0, 53.5, 50.9, 31.4, 30.4, 29.1, 29.1, 29.1, 28.8, 28.7, 26.1, 25.8, 25.0, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 823.7, calcd for $C_{52}H_{61}N_3O_6$ (*m*/*z*), 824.08. Anal. Calcd for $C_{52}H_{61}N_3O_6(H_2O)_{1.5}$: C, 73.32; H, 7.52; N, 4.94. Found: C, 73.28; H, 7.42; N, 4.78.

(*N*,*N*′-Dicyclohexyl-1-dodecyloxy-7-cyclohexylamino)perylene-3,4;9,10-tetracarboxydiimide (10). **2** (88 mg) was added to cyclohexylamine (7 mL). The reaction mixture was heated to 90 °C and kept at this temperature overnight. Then the reaction mixture was cooled to room temperature, and the excess cyclohexylamine was evaporated under reduced pressure. The deep green residue was purified by column chromatography on silica gel with chloroform as eluent. The first green fraction was collected, and the solid was recrystallized from chloroform and methanol to give product **10** as deep green solid (44 mg, yield 51%): mp >280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.68 (s, 1H), 6.19 (d, 1H), 5.03 (m, 2H), 3.95 (t, 2H), 3.65 (br, 1H), 2.55 (m, 6H), 2.15 (m, 2H), 1.94 (m, 4H), 1.82−1.25 (m, 48H), 0.89 (t, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 163.5, 163.4, 163.2, 162.7, 154.8, 145.0, 134.7, 131.2, 128.6, 128.4, 127.9, 125.8, 123.3, 123.2, 121.4, 121.2, 121.0, 120.7, 1201.1, 117.6, 114.7, 69.1, 53.4, 53.3, 51.9, 32.5, 31.4, 29.2, 29.1, 28.9, 28.9, 28.7, 28.5, 26.1, 25.7, 25.2, 25.1, 25.0, 24.4, 22.2, 13.6; MALDI-TOF MS (*m*/*z*) 836.1, calcd for $C_{54}H_{65}N_3O_5$ (*m*/*z*), 836.14. Anal. Calcd for $C_{54}H_{65}N_3O_5$: C, 77.57; H, 7.84; N, 5.03. Found: C, 77.62; H, 7.68; N, 5.15.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **2**−**10**. General experimental section including instruments and methods. Atom coordinates from the AM1 calculation for compounds **3**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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