# **Rainbow Perylene Monoimides: Easy Control of Optical Properties**

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Abstract: Perylene dyes have been widely used as photoreceptors in organic photovoltaics because of their outstanding photo-, thermal and chemical stability as well as their excellent photophysical properties. Herein we describe a novel generation of perylene dyes based on N-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide. The optical properties of these novel perylenes can be finely tuned via the sub-

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stituents in the 1-, 6- and 9-positions of the perylene core. The facile synthesis, tunable orbital and absorption properties, and electrochemical potentials help us to design efficient perylene sensitizers for solar-cell applications.

### Introduction

In the family of colorants, perylene and its derivatives belong to the most important dyes and pigments. Perylene colorants, which have been applied as vat dyes since the be-ginning of the 20th century,<sup>[1]</sup> are widely commercialized due to their outstanding chemical, thermal and photochemical stability, their nontoxicity, and low cost.<sup>[2]</sup> Furthermore, because of their outstanding photophysical properties (for example, high molar absorptivities and fluorescence quantum yields), perylene dyes have been extensively investigated as active components in organic field-effect transistors,<sup>[3]</sup> organic photovoltaic cells,<sup>[4]</sup> dye lasers,<sup>[5]</sup> light-harvesting complexes<sup>[6]</sup> and bio-labels.<sup>[7]</sup>

Since Tang's discovery of organic heterojunction-based photovoltaics using perylene derivatives as n-type semiconductors in 1986,<sup>[4a]</sup> perylene dyes have been increasingly in-

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vestigated in solar cells. In 1997, Gregg and co-workers introduced perylene dyes for dye-sensitized solar cells (DSCs).<sup>[8]</sup> During the last ten years, many perylene chromophores have been used in DSCs.<sup>[9]</sup> Especially, in recent years, our group has developed a promising new type of perylene sensitizer.<sup>[10]</sup> These perylene dyes are based on perylene-3,4-dicarboxyanhydrides (PMAs) substituted in the 9position with diphenylamino, the best of which delivering an unprecedented incident monochromatic photon-to-current conversion efficiency of 87% and yielding a power conversion efficiency of 6.8% under standard AM1.5 solar conditions.<sup>[10b]</sup>

By expanding upon previous methods we describe in this article ways to adjust the HOMO/LUMO energies, the absorption wavelengths  $(\lambda_{max})$  and the spatial properties of the molecular orbitals of perylene dicarboximides (PMIs). For use in DSCs, these PMIs can be saponified to PMAs with anhydride groups which can attach to the TiO<sub>2</sub> surface. With their large  $\pi$ -conjugated systems, PMIs provide a versatile synthetic basis for functionalization not only in the peri but also in the bay positions of the perylene core.<sup>[11]</sup> By using the imide group<sup>[12]</sup> of PMIs as an acceptor and selectively functionalizing the 1-, 6- and 9-positions with different electronic substituents (Figure 1), we have constructed a "pushpull" type family of perylenes, exhibiting a rainbow of colors, tunable spectroscopic and electrochemical properties (Figure 2). These fine-tunings provide a way to new perylene sensitizers with stronger intramolecular charge-transfer (ICT), more suitable HOMO or LUMO energies, and more favorable light absorption properties for solar conversion.



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Figure 1. Perylene dicarboximide (PMI) structure as well as peri and bay substitutions.

variation of bay position



Figure 2. Chemical structures of PMIs.

### **Results and Discussion**

The PMIs can be easily prepared in one or two steps with high yields. The synthesis of compound 1, 2 and 3 were carried out by Buchwald–Hartwig cross-coupling reactions of N-(2,6-diisopropylphenyl)-9-bromoperylene-3,4-dicarbox-

imide (13) with  $N^{1}$ -(4-(dimethylamino)phenyl)- $N^{4}$ , $N^{4}$ -dimethylbenzene-1,4-diamine (12), bis(4-(10*H*-phenothiazin-10-yl)phenyl)amine (9) or  $N^{3}$ , $N^{3}$ , $N^{7}$ , $N^{7}$ -tetramethyl-10*H*-phenothiazine-3,7-diamine (11), respectively. Compounds 4 and 5 were obtained by nucleophilic substitution<sup>[13]</sup> of *N*-(2,6-diisopropylphenyl)-1,6,9-tribromo-perylene-3,4-dicarbox-imide with thiophenol (for 4) or 4-mercaptopyridine (for 5) in the 1,6-positions of PMIs under basic conditions followed by the above mentioned cross-coupling reaction in the 9-position with  $N^{1}$ -(4-(dimethylamino)phenyl)- $N^{4}$ , $N^{4}$ -dimethylbenzene-1,4-diamine (12) (see Scheme 1).

A concept which is particularly important for the analysis of the resulting push-pull substituted PMIs is "orbital partitioning" (OP). Orbital partitioning occurs when on the donor part of the molecule the HOMO coefficients are

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high, while on the acceptor part of the same molecule the coefficients of the LUMO are high. This concept has recently been proven of great value in the design of sensitizer dyes for solar cells:<sup>[14]</sup> 1) Nearly all the ruthenium sensitizers show favorable orbital partitioning (HOMO is localized on the isothiocyanate ligands) and LUMO is localized near the anchor groups (bipyridine ligands).<sup>[15]</sup> Many organic metalfree dyes which have very promising solar-cell performance also have similar orbital properties.<sup>[16]</sup> 2) Strong orbital partitioning can increase the rate of charge injection from the LUMO of the dye to the conduction band of TiO<sub>2</sub>.<sup>[17]</sup> 3) It has also been proven that orbital partitioning resulting in charge separation yields a lower charge recombination rate between electrons in TiO<sub>2</sub> and dve cations.<sup>[18]</sup> Here, we describe a way to achieve perylene dyes with further orbital partitioning and HOMO/ LUMO energy tuning for potentially better solar cell performance.

The frontier orbitals<sup>[19]</sup> of these dyes are calculated at the

RHF/6-31G<sup>\*\*</sup> level.<sup>[20]</sup> Compounds **1**, **4** and **5** exhibit very similar OP properties with the LUMO localized on the perylene core and the HOMO predominantly localized on the amine substituents (Figure 3). The thioether groups in the perylene 1-, 6-positions have only a minor influence on the frontier orbitals of the molecules. Compound **4** has two phenylthio groups in the 1,6-positions whereas **5** has two pyridylthio groups in the same positions. However, the HOMO and LUMO orbitals of both **4** and **5**, are more or less the same as those of compound **1** which has no subsitutents in the *bay* region. Clearly, the orbital partitioning in PMIs is mostly affected by the strong electron donating group in the *peri* positions tune the optical properties as well. The details will be discussed in the following section.

Compared with the orbital similarities of 1, 4 and 5, compounds 2 and 3 exhibit an important difference in orbital partitioning, which results from the different donor ( $N^{1}$ -(4-(dimethylamino)phenyl)- $N^{4}$ , $N^{4}$ -dimethylbenzene-1,4-diamine (1, 4 and 5), bis(4-(10*H*-phenothiazin-10-yl)phenyl)amine (2) or  $N^{3}$ , $N^{3}$ , $N^{7}$ , $N^{7}$ -tetramethyl-10*H*-phenothiazine-



Scheme 1. Synthesis of 1, 2, 3, 4 and 5: i) 6,  $Boc_2O$ , dimethylaminopyridine, THF, reflux, 24 h, 96%; ii) 7, phenothiazine,  $[Pd_2(dba)_3]$ , tri-*tert*-butylphosphine, NaOtBu, anhydrous toluene, reflux, 90 min, 82%; iii) 8, acetic acid, reflux, overnight, 82%; iv) 10, NaOH, THF, methanol, reflux, (product 11 was not purified, directly used for next step reaction); v)  $[Pd_2(dba)_3]$ , tri-*tert*-butylphosphine, NaOtBu, anhydrous toluene, (12, 13, 80°C, overnight, 60%, for 1), (9, 13, 80°C, overnight, 81%, for 2), (11, 13, reflux, 1 h, 17%, for 3), (12, 15, 80°C, overnight, 70%, for 4), (12, 16, 80°C, overnight, 60%, for 5); vi) 14, K<sub>2</sub>CO<sub>3</sub>, NMP, (thiophenol, RT 3 h, 56%, for 15), (4-mercaptopyridine, -20°C, 3 h, 50%, for 16).

3,7-diamine (3) groups in the *peri* position of PMIs (Figure 3). In the case of 3, the LUMO is entirely localized on the perylene core, while the HOMO is entirely localized on the phenothiazine substituent. Secondly, the phenothiazine group is twisted and nearly vertical to the perylene plane. However, with bis(diphenothiazinephenyl) amine as the electron-donating group, both HOMO and LUMO of 2 are localized on the perylene core and correspond to the orbitals of unsubstituted PMI.

Table 1 gives an overview of the measured electrochemical and spectroscopic properties of these PMIs. The absorption spectra of these PMIs in  $CH_2Cl_2$  are shown in Figure 4. By analysis of the HOMO and LUMO potentials, the following effects of *bay* and *peri* substitution can be derived: i) in all compounds, the LUMO potential varies only moderately (between 3.5 eV in 2 and 3.7 eV in 5), reflecting the fact that the LUMO, in all cases, is located on the perylene core and the dicarboximide groups (Figure 3); ii) varying the donor in the *peri*-position (compounds 1, 2 and 3) has a pronounced effect on the HOMO potential, in line with the strong differences noted above and shown in Figure 3. With the HOMO located entirely on the donor moiety, **3** has the lowest potential against oxidation (4.5 eV), whereas **2**, with only minor contributions of the donor to the HOMO, has the highest value (5.0 eV). Compound **1**, where the HOMO is distributed over both subunits, represents an intermediate case (4.8 eV); iii) preserving the *peri* substituent and changing the *bay* substituents (compounds **1**, **4** and **5**) reveals that the phenylthio raises the HOMO (4.6 eV) while leaving the LUMO unchanged with respect to compound **1**; iv) the pyridylthio substituent in the bay slightly narrows the band gap by 0.2 eV relative to **1**.

Concerning the absorption characteristics of the PMI series, compounds 1-5 appear blue, purple, yellow, green and black to the human eye, with absorption maxima 668, 548, 515, 681 and 736 nm in CH<sub>2</sub>Cl<sub>2</sub>, respectively (Figure 4 and Table 1). The corresponding absorption coefficients  $(\varepsilon_{\text{max}})$  are 14410, 31322, 22671, 17575 and 17098  $\text{m}^{-1}$  cm<sup>-1</sup>. These values are higher than those of ruthenium complexes  $(1.4 \times 10^4 \,\mathrm{m^{-1} \, cm^{-1}})$ . As a thin film, compound 5 appears black, and its absorption spectrum overlaps with the whole visible region and part of NIR with a shoulder end at 1100 nm (Figure S10). Therefore, a drastic bathochromic shift can be achieved by relatively simple modifications of the PMI chromophore. With the same peri substitutions, all the absorption spectra of 1, 4 and 5 have two bands which correspond to the CT band (donor to pervlene) at 668 to 736 nm and the perylene  $\pi$ - $\pi$ \* transition at around 500 nm. It is known that the additional bay substituents suppress the aggregation of PMI core and give a redshifted absorption and a higher molar absorption coefficient.<sup>[10a]</sup> With the pyridylthio groups in the *bay* positions, **5** shows a larger  $\lambda_{max}$ (736 nm) than 4 (681 nm) which has phenylthio groups in the *bay*. Concerning the  $\lambda_{max}$  of **1**, **4** and **5**, the Hammett constant,  $^{[23]}\sigma_{\!_{D}}$  is 0.00 for 1 (hydrogen atom), 0.07 for 4 (thiophenyl) and 0.40 for 5 (pyridylthio) and this reflects the  $\lambda_{max}$ variation 668 < 681 < 736 nm. Compared to compounds 1, 4 and 5, the derivatives with alternative peri substituents 2 and 3 do not exhibit the intramolecular CT band (Figure 4). In 2, the optical transition corresponds to the  $\pi$ - $\pi$ \* (HOMO-LUMO) excitation on the PMI moiety, with the HOMO ( $\pi$ ) only slightly disturbed by the *peri*-donor (Figure 3). The  $\lambda_{max}$  therefore is only slightly higher than that of unsubstituted PMI.<sup>[24]</sup> In the case of 3, with complete orbital partitioning between the HOMO and LUMO, the corresponding intramolecular CT transition has effectively zero intensity, because there is essentially no spatial overlap between HOMO and LUMO. The reason for this is the strong twist of the *peri*-donor with respect to the perylene plain ( $\approx 80^\circ$ ) so that the two subunit orbitals do not mix anymore. This explanation is underscored by quantum mechanical calculation of the excitation spectrum by time-dependent density functional theory at the B3LYP/TZVP level:<sup>[25]</sup> The HOMO-LUMO (intramolecular CT) excitation is predicted at  $\approx 1000$  nm but with an oscillator strength close to zero. The calculation predicts a strong absorption at

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Figure 3. Schematic representation of the HOMOs and LUMOs of 1, 2, 3, 4 and 5: partial, no and strong orbital partitioning (RHF/6-31G\*\*).



Figure 4. Absorption spectra of the PMI series in CH<sub>2</sub>Cl<sub>2</sub>.

503 nm, corresponding to the  $\pi$ - $\pi$ \* transition on the PMI moiety. This is actually the HOMO-2 to LUMO excitation. The electrochemical gap ( $E_{\rm gap}$ ) of **3** therefore is the smallest, but the observed optical gap is the largest one in the present series.

# Conclusion

In conclusion, we have successfully designed and synthesized a series of novel perylene dyes with controllable optical and electrochemical properties, which becomes possible

Table 1.  $\lambda_{\text{max}}$  values of PMIs in CH<sub>2</sub>Cl<sub>2</sub>; HOMO/LUMO and their gaps ( $E_{\text{gap}}$ ).

PMIs	$\lambda_{\max}$ [nm]	$\varepsilon_{\rm max} \left[ {\rm M}^{-1} {\rm cm}^{-1}  ight]$	$E_{\rm HOMO}/E_{\rm LUMO}  [{\rm eV}]^{[{\rm a}]}$	$E_{\rm gap}  [{\rm eV}]^{[{\rm b}]}$
3	515	22 671	4.5/3.6	0.9
2	548	31 322	5.0/3.5	1.5
1	668	14410	4.8/3.6	1.2
4	681	17 575	4.6/3.6	1.0
5	736	17098	4.7/3.7	1.0

[a] HOMO (the first oxidation peak onset<sup>[21]</sup>) LUMO (the first reduction peak onset) energies of the dyes were measured under the following conditions: 0.1 M tetrabutylammonium hexaflourophosphate (TBAPF<sub>6</sub>) in dry CH<sub>2</sub>Cl<sub>2</sub>, a Pt working electrode, a platinum wire as counter electrode, and the reference electrode was a silver wire calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal reference.<sup>[22]</sup> [b] The energy gap,  $E_{gap}$  is estimated from the balance of  $E_{HOMO}$  and  $E_{LUMO}$ .

by different *bay* and *peri* substituents. In a simplified view, the *peri* groups coarsely tune the spectroscopic and electrochemical properties of PMIs, whereas the *bay* functional groups provide an additional fine tuning. The remarkable bathochromic shifts obtained by using the *bay* and *peri* functional groups suggest efforts towards even stronger bathochromic shifts and broad absorptions of not only perylene but even higher homologues of PMIs. The different colors, broad absorptions and high nonlinear optical effects of the new dyes qualify them as sensitizers for colorants, organic photovoltaic cells and nonlinear optics, and corresponding investigation will be published in future articles.

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**General methods:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AMX250, Bruker AC300, AMX500 NMR and AMX700 NMR spectrometers using the residual proton or the carbon signal of the deuterated solvent as an internal standard. Chemical shifts are reported in parts per million. FD mass spectra were performed with a VG-Instrument ZAB 2-SE-FDP. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University.

**Materials**: Tetrahydrofuran (Fluka) and toluene (Fluka) were distilled over sodium/benzophenone. Tris(dibenzylideneacetone)dipalladium(0) [Pd<sub>2</sub>(dba)<sub>3</sub>] were purchased from Aldrich.  $N^1$ -(4-(Dimethylamino)phenyl)- $N^4$ , $N^4$ -dimethylbenzene-1,4-diamine, benzoyl leuco methylene blue and phenothiazine were purchased from ABCR GmbH. Column chromatography was performed with dichloromethane (chromasolv, Riedel), methanol, pentane or toluene on silica gel (Geduran Si60, Merck). N-(2,6-Diisopropylphenyl)-perylene-3,4-dicarboximide and N-(2,6-diisopropylphenyl)-9-bromo-perylene-3,4-dicarboximide were supplied from BASF-AG (Ludwigshafen). N-(2,6-Diisopropylphenyl)-1,6,9tribromo-perylene-3,4-dicarboximide was synthesized as described before.<sup>[13a]</sup> All reported yields are isolated yields.

**General procedure**: Buchwald–Hartwig cross-coupling reactions: A mixture of 9-bromoperylene dicarboximide (1 equiv), amine (1. equiv), tris-(dibenzylideneacetone) dipalladium(0) (5 % equiv), tri-*tert*-butylphosphine (10 % equiv), sodium-*tert*-butyl alcohol (1.5 equiv) and dry toluene was stirred at 80 °C in an argon atmosphere overnight. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

*N*-(2,6-Diisopropylphenyl)-9-di(*p*-dimethylamino-phenyl)aminoperylene-3,4-dicarboximide (1): Compound 1 was obtained by general Buchwald– Hartwig reaction conditions (250 mg of *N*-(2,6-diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide). Column chromatography using dichloromethane/methanol 20:1 on silica gave 1 as a blue solid (200 mg, 60%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$ =8.58 (t, 2H), 8.45 (d, *J*=8 Hz, 2H), 8.34 (t, 2H), 8.14 (d, *J*=8 Hz, 1H), 7.47 (m, 2H), 7.36 (d, *J*=8 Hz, 2H), 7.22 (d, *J*=8 Hz, 1H), 6.93 (d, *J*=9 Hz, 4H), 6.68 (d, *J*=9 Hz, 4H), 2.91 (s, 12H), 2.76 (m, 2H), 1.15 ppm (d, *J*=7 Hz, 12H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K)  $\delta$ =164.73, 147.73, 146.75, 138.60, 132.52, 132.43, 132.27, 129.99, 129.72, 129.12, 127.21, 126.58, 125.52, 124.50, 121.16, 120.38, 119.95, 119.62, 114.07, 41.27, 29.40, 24.28 ppm; FD mass spectrum (8 kV): *mlz* (%): calcd for 734.95; found: 735.0 (100) [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>50</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>: C 81.71, H 6.31, N 7.62; found: C 80.95, H 6.32, N 6.92.

**N-Boc-di(4-bromophenyl) amine (7)**: A mixture of di(4-bromophenyl)amine (4.0 g, 12.23 mmol), (Boc)<sub>2</sub>O (2.93 g, 13.45 mmol, 1.1 equiv), dimethylaminopyridine (300 mg, 2.45 mmol, 0.2 equiv), and dry THF (20 mL) was refluxed for 24 h under argon. After cooling to room temperature, the mixture was filtered to get white solid. After washed by THF once and dried, white crystals were obtained (5 g, 96%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$ =7.44 (d, J=8 Hz, 4H), 7.11 (d, J=8 Hz, 4H), 1.44 ppm (s, 9H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$ =153.21, 142.30, 132.18, 128.97, 119.39, 82.05, 28.25 ppm; FD mass spectrum (8 kV): *m*/*z* (%): calcd for: 427.14; found: 427.8 (100) [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>17</sub>H<sub>17</sub>Br<sub>2</sub>NO<sub>2</sub>: C 47.80, H 4.01, N 3.28; found: C 47.82, H 4.02, N 3.24.

**N-Boc-di(phenothiazinylphenyl) amine (8)**: To a 100 mL Schlenk flask containing **2a** (5.0 g, 11.7 mmol), phenothiazine (2.7 g, 23.4 mmol), [Pd<sub>2</sub>-(dba)<sub>3</sub>] (500 mg, 0.585 mmol), tri-*tert*-butylphosphine (118 mg, 0.585 mmol), sodium-*tert*-butoxide (3.9 g, 40.3 mmol) and anhydrous toluene (50 mL) were added under argon atmosphere. The mixture was refluxed for 90 min. The hot reaction mixture was filtered in order to remove insoluble solids. The filtrate was concentrated under reduced pressure to give a white powder. The crude product was purified by silica column chromatography eluted with dichloromethane/pentane 2:1 to yield **8** as a white powder (6.4 g, 82 %). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$ =7.53 (d, *J*=8 Hz, 4H), 7.40 (d, *J*=8 Hz, 4H), 7.02 (d, *J*=

7 Hz, 4H), 6.87 (m, 8H), 6.34 (d, J=7 Hz, 4H), 1.51 ppm (s, 9H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$ =153.84, 144.68, 142.94, 139.06, 131.25, 129.65, 127.48, 127.28, 123.24, 121.26, 117.00, 82.22, 28.46 ppm; FD mass spectrum (8 kV): m/z (%): calcd for: 663.87; found: 664.4 (100%) [M]<sup>+</sup>; elemental analysis calcd (%) for C<sub>41</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C 74.18, H 5.01, N 6.33, S 9.66; found: C 74.16, H 5.11, N 6.18, S 9.68.

**Di(phenothiazinylphenyl) amine (9):** Compound **8** (2.6 g, 3.92 mmol) was dissolved in acetic acid (60 mL) and the solution was refluxed overnight. After cooling to room temperature, the mixture was filtered to get white crystal. After washed by acetic acid once and dried, a white solid was obtained (1.8 g, 82 %). <sup>1</sup>H NMR (250 MHz, THF, 300 K):  $\delta$ =7.99 (s, 1 H), 7.42 (d, *J*=8 Hz, 4H), 7.31 (d, *J*=8 Hz, 4H), 6.93 (d, *J*=8 Hz, 4H), 6.75 (m, 8H), 6.32 ppm (d, *J*=8 Hz, 4H); <sup>13</sup>C NMR (62.5 MHz, THF, 300 K):  $\delta$ =145.93, 144.56, 134.13, 133.00, 127.71, 127.39, 123.13, 120.93, 120.01, 116.77 ppm; FD mass spectrum (8 kV): *m/z* (%): 563.75; found. 564.2 (100) [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>36</sub>H<sub>25</sub>N<sub>3</sub>S<sub>2</sub>: C 76.70, H 4.47, N 7.45, S 11.38; found: C 76.72, H 4.56, N 7.36, S 11.36.

#### N-(2,6-Diisopropylphenyl)-9-di(phenothiazinylphenyl)amino-perylene-

**3,4-dicarboximide** (2): Compound 2 was obtained by general Buchwald-Hartwig reaction condition (800 mg of *N*-(2,6-diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide). Columnchromatography using dichloromethane on silica gave 2 as a violet solid (1.2 g, 81 %). <sup>1</sup>H NMR (250 MHz, THF, 300 K):  $\delta$  = 8.67–8.50 (m, 4H), 8.19 (d, *J* = 8 Hz, 1H), 7.67 (d, *J* = 8 Hz, 1H), 7.54–7.14 (m, 14H), 7.03–6.80 (m, 12H), 6.38 (d, *J* = 8 Hz, 4H), 2.77 (m, 2H), 1.16 ppm (d, *J* = 7 Hz, 12H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  = 164.59, 147.99, 146.71, 146.46, 144.97, 138.53, 137.97, 137.76, 136.02, 132.51, 132.47, 132.35, 132.16, 131.19, 130.60, 129.53, 128.72, 128.29, 128.07, 127.45, 127.23, 125.79, 124.93, 123.10, 121.79, 121.46, 120.86, 116.66, 29.63, 24.28 ppm; FD mass spectrum (8 kV): *m/z* (%): calcd for 1043.33; found: 1045.3 (100) [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>70</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C 80.59, H 4.83, N 5.37, S 6.15; found: C 80.76, H 5.05, N 5.23, S 6.19.

#### N-(2,6-Diisopropylphenyl)-9-(3,7-dimethylamino-phenothiazine-10-yl)-

perylene-3,4-dicarboximide (3): A mixture of benzoylleucomethylene blue (1.5 g, 3.8 mmol), NaOH (310 mg, 3.8 mmol), THF (5 mL) and MeOH (15 mL) was stirred and refluxed in a 250 mL mono-necked round flask for 12 h. After the temperature of the mixture was cooled down to room temperature, the solvent was removed by bubbling with argon. Then N-(2,6-diisopropylphenyl)-9-bromoperylene-3,4-dicarboximide (1.5 g, 3.1 mmol), [Pd<sub>2</sub>(dba)<sub>3</sub>] (123 mg, 0.13 mmol), tri-tert-butylphosphine (27 mg, 0.13 mmol) and sodium tert-butoxide (12 mg, 0.13 mmol) and 100 mL of anhydrous toluene were added into the reaction mixture under argon atmosphere. The suspension was refluxed for 1 h. The mixture was concentrated under reduced pressure. The crude product was purified by silica column chromatography eluted with dichloromethane/MeOH 20:1 to give 3 as a brown powder (500 mg, 17%). <sup>1</sup>H NMR (250 MHz, DMF, 300 K):  $\delta = 9.07$  (d, J = 8 Hz, 1 H), 8.98 (d, J =8 Hz, 1 H), 8.91 (d, J=8 Hz, 1 H), 8.88 (d, J=8 Hz, 1 H), 8.68 (d, J=8 Hz, 1 H), 8.64 (d, J = 8 Hz, 1 H), 8.31 (d, J = 8 Hz, 1 H), 8.03 (d, J = 8 Hz, 1 H), 7.79 (t, 1H), 7.50 (t, 1H), 7.41 (d, J=8 Hz, 2H), 6.61 (d, J=4 Hz, 2H), 6.35 (d, J=9 Hz, 2H), 6.25 (d, J=8 Hz, 2H), 2.85 (m, 2H), 2.82 (s, 12H), 1.15 ppm (d, J = 7 Hz, 12 H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta =$ 164.61, 147.38, 146.74, 137.92, 137.61, 132.51, 132.46, 132.16, 131.15, 129.88, 128.58, 127.47, 125.12, 124.59, 121.91, 121.81, 121.47, 121.26, 41.83, 29.67, 24.30 ppm; FD mass spectrum (8 kV): m/z (%): calcd for: 765.00; found: 765.3 (100)  $[M]^+$ ; elemental analysis calcd (%) for C<sub>50</sub>H<sub>44</sub>N<sub>4</sub>O<sub>2</sub>S: C 78.50, H 5.80, N 7.32, S 4.19; found: C 78.50, H 5.76, N 7.31, S 4.22.

 $N\-(2,6\-Diisopropylphenyl)\-1,6\-diphenylthio\-9\-bromoperylene\-3,4\-dicar-$ 

**boximide (15):** N-(2,6-Diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (1 g, 1.39 mmol), thiophenol (153 mg, 1.39 mmol) and potassium carbonate (128 mg, 1.39 mmol) were stirred in NMP (80 mL) at room temperature. After 1.5 h, additional thiophenol (76 mg, 0.6 mmol) and potassium hydrate (128 mg, 1.39 mmol) were added into the reaction mixture. The mixture was stirred at the same temperature for another 1.5 h. After cooling down to room temperature, the reaction mixture was poured into a mixture of water and HCl 4:1. The resulting precipitate was washed by water and dried. The product was purified by column chromatography on silica gel using dichloromethane/pentane 1:4 to give

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a dark red solid (600 mg, 56 %). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta =$  8.63 (d, J = 8 Hz, 1H), 8.50–8.41 (m, 4H), 8.11 (d, J = 8 Hz, 1H), 7.91 (t, 1H), 7.47–7.26 (m, 13 H) 2.64 (m, 2H), 1.07 ppm (d, J = 7 Hz, 12 H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta =$  163.88, 146.51, 136.02, 135.77, 135.49, 135.40, 135.10, 133.35, 133.31, 131.75, 131.70, 131.29, 131.10, 130.30, 129.83, 129.33, 128.61, 128.09, 127.32, 125.95, 125.83, 124.45, 120.95, 29.55, 24.17 ppm; FD mass spectrum (8 kV): m/z (%): calcd for 776.82; found: 775.5 (100) [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>40</sub>H<sub>34</sub>BrNO<sub>2</sub>S<sub>2</sub>: C 71.12, H 4.41, N 1.80, S 8.26; found: C 70.79, H 4.56, N 1.73, S 7.93.

N-(2,6-Diisopropylphenyl)-1,6-diphenylthio-9-di(p-dimethylaminophenyl)aminoperylene-3,4-dicarboximide (4): Compound 4 was obtained by general Buchwald-Hartwig reaction condition (115 mg of N-(2,6-diisopropylphenyl)-1,6-diphenylthio-9-bromoperylene-3,4-dicarboximide). Column chromatography using dichloromethane/methanol 20:1 on silica gave 4 as a green solid (100 mg, 70%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta =$ 8.60 (d, J=8 Hz, 1 H), 8.46 (m, 2 H), 8.27 (d, J=8 Hz, 1 H), 7.54-7.25 (m, 16H), 6.99 (d, J=9 Hz, 4H), 6.70 (d, J=9 Hz, 4H), 2.92 (s, 12H), 2.66 (m, 2H), 1.08 ppm (d, J=7 Hz, 12H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta = 164.08, 147.91, 146.60, 140.29, 137.38, 136.58, 136.49, 136.28,$ 135.45, 134.09, 132.85, 132.11, 132.05, 130.74, 130.17, 130.07, 129.73, 128.94, 128.70, 128.54, 128.37, 126.62, 125.82, 125.74, 124.75, 124.42, 123.31, 123.06, 120.39, 119.25, 114.04, 41.24, 29.55, 24.19 ppm. FD mass spectrum (8 kV): m/z (%): calcd for 951.28; found: 950.4 (100) [M]+; elemental analysis calcd (%) for C<sub>62</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C 78.28, H 5.72, N 5.89, S 6.74; found: C 77.46, H 5.78, N 5.74, S 6.55.

N-(2,6-Diisopropylphenyl)-1,6-di(4-thiopyridineyl)-9-bromoperylene-3,4dicarboximide (16): N-(2,6-diisopropylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (1 g, 1.39 mmol), 4-mercaptopyridine (310 mg, 2.78 mmol) and potassium carbonate (340 mg, 2.78 mmol) were stirred in NMP (80 mL) at -20 °C for 3 h. The reaction mixture was poured into a mixture of water. The resulting precipitate was washed by water and dried. The product was purified by column chromatography on silica gel using dichloromethane to give a dark red solid (500 mg, 50 %). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ=8.82-8.79 (m, 3 H), 8.60 (d, J=8 Hz, 1 H), 8.46-8.35 (m, 5H), 8.01 (d, J=8 Hz, 1H), 7.81 (t, 1H), 7.46 (t, 1H), 7.35 (d, J=8 Hz, 2 H), 7.04 (d, J=6 Hz, 4 H), 2.72 (m, 2 H), 1.13 ppm (d, J= 7 Hz, 12 H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta = 163.49$ , 150.65, 148.01, 146.52, 140.06, 131.84, 131.39, 131.09, 131.06, 130.83, 130.62, 130.47, 130.11, 129.07, 128.72, 127.83, 127.53, 127.27, 124.65, 122.75, 122.66, 121.52, 121.48, 29.68, 24.249 ppm; FD mass spectrum (8 kV): m/z (%): calcd for 779.9; found: 778.80 (100) [M]+; elemental analysis calcd (%) for  $C_{44}H_{32}BrN_3O_2S_2$ : C 67.86, H 4.14, N 5.40, S 8.23; found: C 67.86, H 4.29, N 5.34, S 8.24.

*N*-(2,6-Diisopropylphenyl)-1,6-di(4-thiopyridinyl)-9-di(*p*-dimethylaminophenyl)aminoperylene-3,4-dicarboximide (5): Compound 5 was obtained by general Buchwald–Hartwig reaction condition (70 mg of *N*-(2,6-diisopropylphenyl)-1,6-di(4-thio-pyridine-yl)-9-bromo-perylene-3,4-dicarbox-

imide). Column chromatography using dichloromethane/methanol 20:1 on silica gave **5** as a black solid (50 mg, 60%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  = 8.77–8.71 (m, 3H), 8.61 (d, *J* = 8 Hz, 1H), 8.33 (m, 4H), 8.17 (d, *J* = 8 Hz, 1H), 7.52–7.31 (m, 4H), 7.08–7.01 (m, 5H), 6.88 (d, *J* = 9 Hz, 4H), 6.67 (d, *J* = 9 Hz, 4H), 2.92 (s, 12H), 2.73 (m, 2H), 1.11 ppm (d, *J* = 7 Hz, 12H); <sup>13</sup>C NMR (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  = 163.76, 150.97, 150.46, 150.39, 148.98, 148.86, 148.14, 146.60, 141.55, 141.19, 139.79, 132.85, 131.80, 131.60, 131.31, 130.51, 129.95, 129.59, 128.16, 127.55, 126.75, 126.11, 124.58, 122.71, 122.29, 121.97, 121.68, 120.71, 119.24, 113.91, 41.12, 29.65, 24.25 ppm; FD mass spectrum (8 kV): *m*/*z* (%): calcd for 953.25; found: 954.5 (100) [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>60</sub>H<sub>52</sub>N<sub>6</sub>O<sub>5</sub>S<sub>2</sub>: C 75.60, H 5.50, N 8.82, S 6.73; found: C 75.53, H 5.63, N 8.81, S 6.86.

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   [22] Cyclic voltammetry for spectroelectrochemistry experiments was
- [22] Cyclic Voltammerty for spectroelectroelectroelemistry experiments was carried out with an EG&G Princeton Applied Research potentiostat, model 273. The working electrode consisted of an inlaid platinum disk (1.5 mm diameter) that was polished on a felt pad with 0.05 µm alumina and sonicated in milli-Q water for 5 min before each experiment. A platinum wire was used as the counter electrode

and an Ag wire was used as the reference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) in the measurement. The CV measurements were carried out in a solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1 m) in dry CH<sub>2</sub>Cl<sub>2</sub> with a scan rate of 50 mV s<sup>-1</sup> at room temperature under argon.

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