Organic LETTERS
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Toward Perylene Dyes by the Hundsdiecker Reaction

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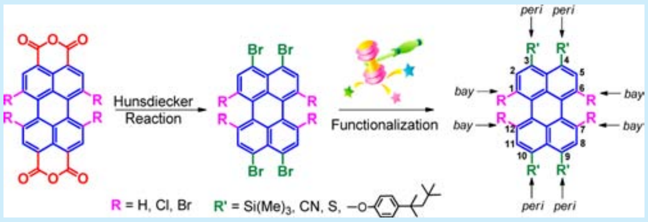
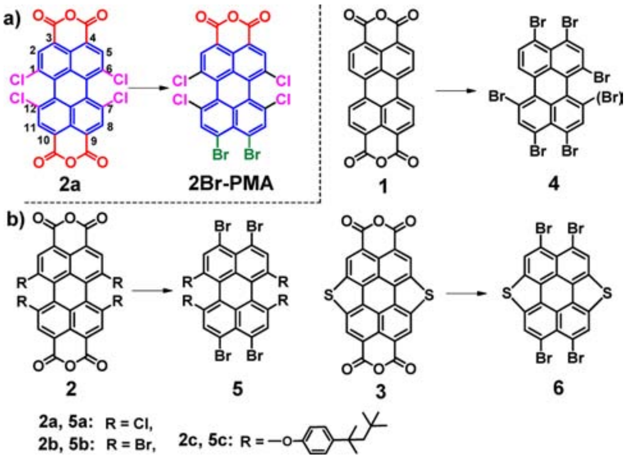
Ⓢ *Supporting Information*

ABSTRACT: An efficient method to synthesize 3,4,9,10-tetrabromoperylenes is reported under optimized Hunsdiecker conditions. Various octasubstituted perylenes were obtained by reaction of 1,6,7,12-tetrachloro-3,4,9,10-tetrabromoperylene with phenol, trimethylsilyl chloride, cooper cyanide, or sulfur via metal-catalyzed couplings or nucleophilic substitutions. These new perylenes show completely different optical and redox properties, thus opening a facile way to develop new chromophophore structures.



Perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs), which have served as famous dyes, pigments,[1] and semiconductors[2,3] with various applications,[4−7] are normally synthesized via perylene-3,4,9,10-tetracarboxylic acid dianhydrides (PDA **1**, Scheme 1) with amines in nitrogen-containing polar solvents (e.g., quinoline, imidazole, and *N*-methyl-2-pyrrolidone) or acidic solutions (e.g., acetic acid and propanoic acid). On the other hand, under harsh imidization conditions in quinoline with Zn(OAc)$_2$, **1** can be directly transformed into perylene monoimides (PMIs) with reasonable yields.[8] Higher homologues of perylene diimides, for instance, terylene diimides[9] and quaterylene diimides,[10] have been synthesized in the last several decades using PMIs as starting materials. Additionally, PMIs can be either monobrominated (in the 9-position) or tribrominated (in the 1,6,9-positions).[11] In particular, 9-functionalized PMIs are currently under intensive investigation for application in dye-sensitized solar cells.[12]

Scheme 1. Our Previous Work (a) and the Present (b) Synthesis of 3,4,9,10-Tetrabromo-Substituted Perylenes[a]



[a]General procedure toward compounds **4** (67%), **5a** (83%), **5b** (83%), **5c** (6%), and **6** (89%): NaOH, water, Br$_2$, 70 °C, 30 min; **5c**: NaOH, water, THF, Br$_2$, rt.

However, until now, only a limited number of perylenes without carboximides in the 3,4,9,10-positions have been synthesized (see Scheme 1). 1,6,7,12-Substituted perylenes with substituents other than carboximide units have not yet been realized because direct functionalization of perylene only occurs at the 2,5,8,11-positions.[13] Copper-catalyzed decarboxylation to remove anhydrides and subsequent halogenation are the conventional methods to achieve other functional groups in the *peri*-position of 2,5,8,11-subsituted perylenes.[14a] Another method to achieve decarboxylative halogenation is through use of the Hunsdiecker reaction.[14b] The initial discovery by Hunsdiecker used dry silver(I) salts of aliphatic carboxylic acids in a reaction with bromine, resulting in the formation of alkyl bromides.[14c] We have previously described an efficient way to synthesize 9,10-dibromo-1,6,7,12-tetrachloroperylene-3,4-dicarboxylic acid monoanhydride (2Br-PMA, Scheme 1a) by a selective Hunsdiecker reaction of **2a.**[15] Herein, we report continuous work on a series of symmetric 3,4,9,10-subsituted perylenes via further developed Hunsdiecker reactions, establishing a facile method toward new types of chromophores. It is noteworthy to mention that these 3,4,9,10-substituted perylenes cannot be obtained by the direct functionlization of perylene. On the other hand, the present 3,4,9,10-funtionalization method not only increases the solubility of perylene (e.g., **7**) but also will induce phase-forming properties.

Our synthetic concept uses the Hunsdiecker reaction to remove the tetracarboxylic acid dianhydride groups, while in situ introducing halogens into the four *peri*-positions (Scheme 1b). We selected five perylene dianhydrides as substrates, which

Received: March 22, 2014
Published: May 16, 2014

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were PDA (**1**), 1,6,7,12-tetrachloro-PDA (**2a**), 1,6,7,12-tetrabromo-PDA (**2b**), 1,6,7,12-tetra(*tert*-octylphenoxy)-PDA (**2c**), and the double S-annelated PDA (**3**). The solubility of the anhydrides in basic solutions was a critical issue for the Hunsdiecker reaction. With a flat and rigid core, the unsubstituted PDA **1** and S-annelated PDA **3** are not soluble in most solvents. However, for the present purpose, the substrates must be soluble in aqueous NaOH which is, indeed, the case at 70 °C for all starting compounds except for the tetraphenoxy compound **2c**. For this reason, the desired products **5a**, **5b**, and **6** can be obtained in high yields (>80%). However, without *bay*-substituents, the Hunsdiecker reaction of **1** with bromine is very difficult to control. In this case, the main product is 1,3,4,6(7),9,10-hexabromoperylene **4** with negligible amounts of 3,4,9,10-tetrabromoperylene. Because of the four *tert*-octylphenoxy groups at the 1,6,7,12-positions, **2c** is hardly soluble in aqueous NaOH solution. Therefore, THF was used as cosolvent to obtain a clear solution of **2c** and NaOH in water. Bromine was then added to the mixture at room temperature in order to avoid bromination at the phenoxy groups. Unfortunately, **5c** was obtained only in very low yields (ca. 6%) because most of the starting material **2c** precipitated from the reaction mixture and thus prevented the Hunsdiecker reaction. Among the perylenes (**4**−**6**) discussed above, we are particularly interested in 1,6,7,12-tetrachloro-3,4,9,10-tetrabromoperylene **5a** because of its high solubility and abundant functionalization possibilities.

A single crystal of **5a** was obtained by slow evaporation of its toluene solution. Its crystal structure confirmed the complete bromination at the four *peri*-positions of the perylene (Figure 1a). Compound **5a** possesses a strongly twisted perylene skeleton with a dihedral angle of 38.6° between the two naphthalene planes and an average torsion angle of 40.5° at the perylene *bay*-positions. This could be ascribed to the repulsion between the two *bay*-substituted chlorine atoms. This twisted configuration of **5a** is comparable to that of octachloroperylene diimide, where a dihedral angle of 37.2° between the two naphthalene planes is found.[16] Columnar packing was observed with stacks of molecules oriented along the *c* axis, probably driven by the halogen−π interactions (3.47 Å)[17] between the bromine atoms and adjacent naphthalene planes (Figure 1c). Like other twisted conjugated systems, **5a** exhibits good solubility in common organic solvents. This prompted us to carry out further functionalization.

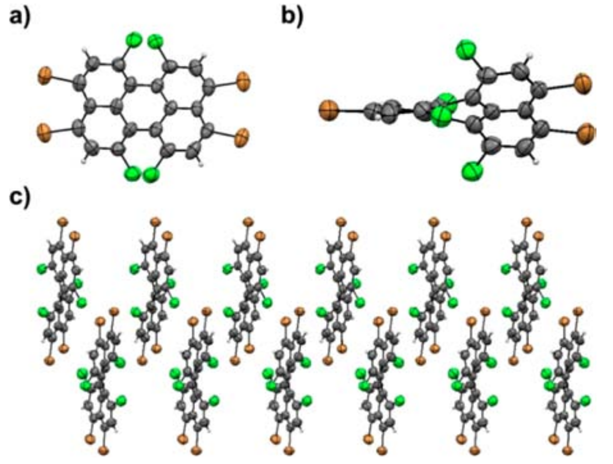
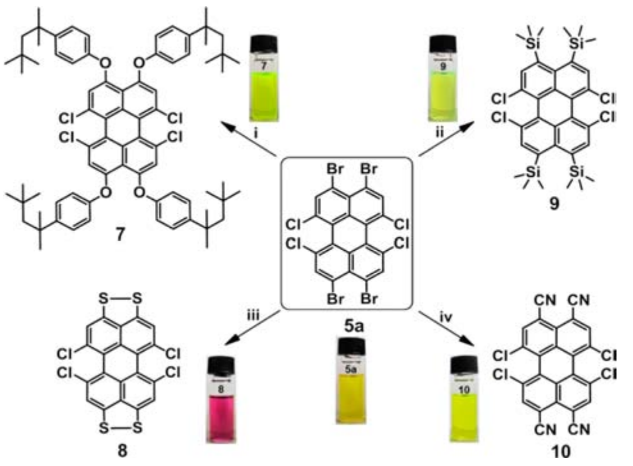


Figure 1. Crystal structure of **5a** obtained. (a) Top and (b) side views shown as ORTEP drawing. (c) Side view of columnar packing diagram along the *c* axis. C, gray; H, white; Cl, green; Br, bronze.

Compound **5a** was reacted with phenol, trimethylsilyl chloride, sulfur, and copper cyanide, respectively. All the reactions took place at the four bromo positions instead of at the chloro sites. Upon synthesis of **7**, conventional phenoxylation conditions were used (Scheme 2).[10] A mixture of 4-*tert*-octylphenol, K_2CO_3, *N*-methyl-2-pyrrolidone (NMP), and compound **5a** was reacted at 120 °C to obtain 1,6,7,12-tetrachloro-3,4,9,10-tetra(*p*-*tert*-octylphenoxy)perylene (**7**) in 74% yield. In addition, the four bromo groups were “protected” with a trimethylsilyl (TMS) group by reacting **5a** with trimethylsilyl chloride to afford the useful intermediate **9** in 48% yield. This offers many possibilities for further useful transformations. By simply treating **5a** with sulfur powder in a polar aprotic solvent (NMP) at 190 °C, the S-annelated perylene **8** was obtained in almost quantitative yield. On the other hand, four strongly electron-withdrawing cyano groups were introduced by electrophilic substitution of **5a** and CuCN in DMF, which afforded tetracyanoperylene **10** in 70% yield.

Scheme 2. Functionalization of 1,6,7,12-Tetrachloro-3,4,9,10-tetrabromoperylene[a]



[a] Key: (i) 4-*tert*-octylphenol, K_2CO_3, NMP, 120 °C, 5 h, 74%; (ii) *n*-BuLi, THF, −78 °C, TMSCl, 2 h, 48%; (iii) sulfur, NMP, 190 °C, 3 h, 97%; (iv) CuCN, DMF, 130 °C, 2 h, 70%; inset: photos of the solution of **5a**, **7**−**10** in CH_2Cl_2.

The UV/vis absorption spectra of perylenes **5a** and **7**−**10** were recorded in CH_2Cl_2 for comparison as shown in Figure 2a. Compound **5a** displayed an absorption maximum at 460 nm with a bathochromic shift of 24 nm when compared to that of the parent perylene (436 nm).[18] After replacement of the bromo groups with octylphenoxyl, trimethylsilyl (TMS), and cyano groups, the absorption maxima were shifted to 468 nm for **7**, 447 nm for **9** ,and 473 nm for **10**, respectively. To our surprise, the S-annelated perylene **8** formed a pink solution in CH_2Cl_2 and exhibited a significant bathochromic shift of 100 nm compared with that of **5a**, with an absorption maximum at 560 nm. The two strong electron-donating disulfur bridges and four electron-withdrawing chloro groups form a donor−acceptor system through the perylene core and thus lead to such a bathochromic shift. Similar to other reported perylenes, compounds **5a** and **7**−**10** are fluorescent. The fluorescence spectra recorded in CH_2Cl_2 are shown in Figure 2b. The photoluminescence of **5a** and **7**−**10** ranged from cyan, green,

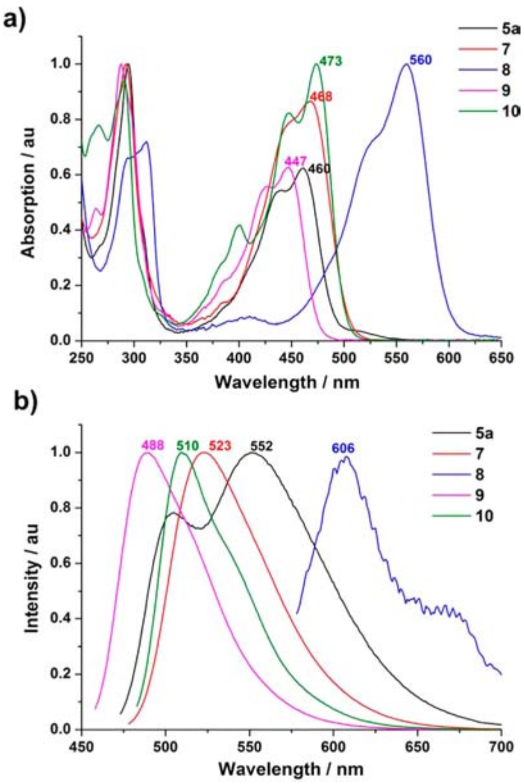


Figure 2. Normalized (a) UV−vis and (b) fluorescence spectra of perylenes **5a** and **7**−**10** in CH_2Cl_2.

yellow, to red depending on their *peri*-substituents. Perylenes **7**, **9**, and **10** displayed intense emission peaks at 523, 488, and 510 nm with fluorescence quantum yields (Φ) of 86%, 99%, and 28%, respectively. In contrast, the sulfur-annulated perylene **8** only exhibited very weak fluorescence at 606 nm. These results indicate that one can conveniently tune the optical properties of the new perylene derivatives by the substituents at the four *peri*-positions, which has not been achieved before.

To elucidate the influence of the substituents in the *peri*-positions on the energy levels of the molecular orbitals, the electrochemical properties of the perylenes **7**−**10** were investigated by cyclic voltammetry (CV) (Figure 3). The onset potentials, together with the calculated values for the HOMO−LUMO energy levels of **7**−**10**, are summarized in Table 1. For example, compounds **7** and **8** both displayed two reversible oxidation curves at 0.55, 0.79 V and 0.13, 0.35 V, respectively, representing the stepwise formation of radical cations and dications upon oxidation. In contrast, the trimethylsilyl-substituted perylene **9** only exhibited one reversible oxidation peak with an onset potential at 0.93 V. Its first oxidation onset was 0.8 V larger than that of **8**, suggesting that **8** was oxidized much more easily than **9**. On the other hand, in the case of tetracyano-substituted perylene **10**, no oxidation peak was observed, while the material instead exhibited two reversible reduction curves at −0.63 and −0.96 V. These results demonstrate a way to tune the electronic properties of perylene from those of a strong donor (i.e., **8**) to a strong acceptor molecule (i.e., **10**). The LUMO energy level of **10**, calculated from the CV measurement, is as low as −4.17 eV, which is lower than that of the well investigated PDI (−3.8 eV)[19] and even comparable to those of fullerene derivatives (e.g., C60: −4.5 eV; PCBM: −3.7 eV).[20] These comparsions suggest that **10** could serve as n-type semiconductor as well as acceptor material in organic solar cells.

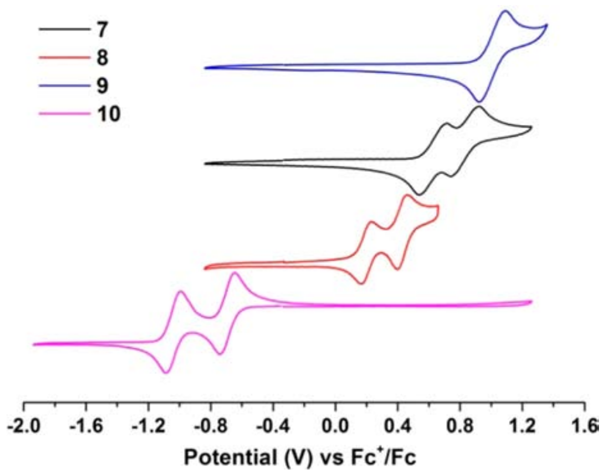


Figure 3. Cyclic voltammograms of **7**−**10** in CH_2Cl_2 (10^{-3} mol L^{-1}); scan rate 100 mVs^{-1}, vs Fc^+/Fc.

Table 1. Optical and Electronic Properties of Perylenes

	λ_{max} (nm)	E_{gap}[a] (V)	E_{red1}[b] (V)	E_{ox1}[b] (V)	LUMO (eV)	HOMO (eV)
7	468	2.46		0.55	-2.89^e	-5.35^d
8	560	2.07		0.13	-2.86^e	-4.93^d
9	447	2.62		0.93	-3.11^e	-5.73^d
10	473	2.48	−0.63		-4.17^c	-6.65^f

[a] Calculated from the onset of UV absorption. [b] Onset potentials, determined by cyclic voltammetric measurements in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 vs Fc^+/Fc. [c] Estimated vs vacuum level from $E_{LUMO} = -4.80$ eV $- E_{red1}$. [d] Estimated vs vacuum level from $E_{HOMO} = -4.80$ eV $+ E_{ox1}$. [e] Calculated from $E_{LUMO} = E_{HOMO} + E_{gap}$. [f] Calculated from $E_{HOMO} = E_{LUMO} - E_{gap}$.

In summary, we have presented the synthesis of 3,4,9,10-tetrabromo-substituted perylenes and their further functionlization with sulfur, phenol, CuCN, and trimethylsilyl chloride. The Hunsdiecker reaction opens a facile and low-cost way to synthesize nonimide perylene chromophores via perylene dianhydrides. The new *peri*-perbrominated and *bay*-subsituted perylenes serve as versatile building blocks to make novel perylene dyes. The potential of these new perylenes for use in high-tech applications, such as OFET and OPV, is currently under investigation in our laboratory. Furthermore, the novel tetrabromoperylene **5a** will serve as a versatile building block to construct rylene-based graphene nanoribbons.[21]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Volkswagen Foundation Project (AZ. 85101-85103) and BASF SE.

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