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New Synthetic Routes to *Z*-Shape Functionalized Perylenes

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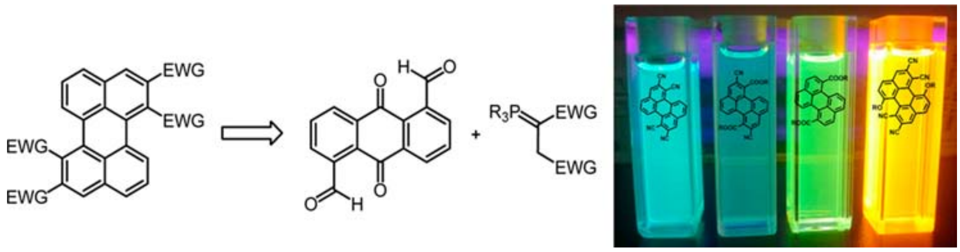
ABSTRACT



Z-shape (1,2,7,8-tetrasubstituted) perylene derivatives are novel chromophores with great potential in various applications. Yet, the synthetic entry into this class of molecules is hitherto quite limited. In this communication, the synthesis of a series of Z-shape perylene derivatives via a double Wittig–Knoevenagel benzannulation protocol is reported. Preliminary photophysical and electrochemical studies indicate that the frontier orbital energy levels of these new perylene systems are modulated by electronic, regiochemical, and conformational effects.

Perylene is an important class of organic chromophores. Although first developed as dyes and pigments,[1] their recent applications have reached far beyond their original role. These molecules are especially versatile in the field of organic electronics where perylene derivatives are frequently employed in devices including field effect transistors,[2] light emitting diodes,[3] photovoltaic cells,[4] optical switches,[5] and molecular wires.[6]

Because of the commercial availability of 3,4,9,10-perylenetetracarboxylic dianhydride, numerous perylene imide and ester derivatives have been synthesized.[7] This substitution pattern is referred to as *linear* or *peri* as depicted in Scheme 1. Recently, researchers have also developed protocols to further functionalize these *linear* derivatives at the *bay* (1,6,7,12) positions *via* halogenation[8] or at the *ortho* (2,5,8,11) positions *via* ruthenium complex catalyzed C–H activation.[9]

On the other hand, the 1,2,7,8-substituted perylene derivative (generally referred to as a *Z*-shape or *ortho-bay* derivative) is quite rare. The only example was published by Meador and co-workers[10] in 2006. The key step in their synthesis is the Diels–Alder trapping of *o*-xylylenols (generated *via* Norrish type II hydrogen abstraction) by maleimides to result in *Z*-shape perylene diimides (PDIs). Since the photochemistry requires an aryl ketone as its substrate, the Z-shape perylene thus produced inevitably carries phenyl substitutions at its *peri* positions. To broaden

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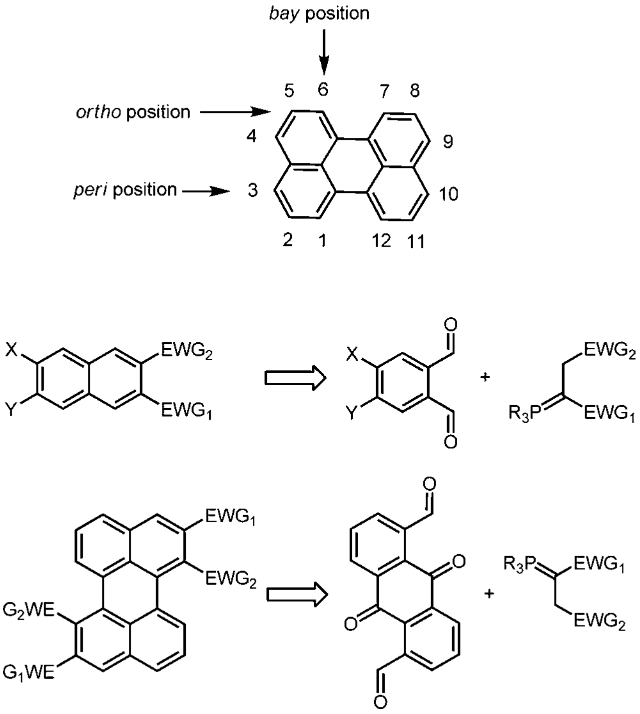
our understanding of this new class of perylenes and to explore their potential applictions, we developed a new synthetic strategy to Z-shape perylene with a much wider substrate scope. The preliminary results are reported herein.

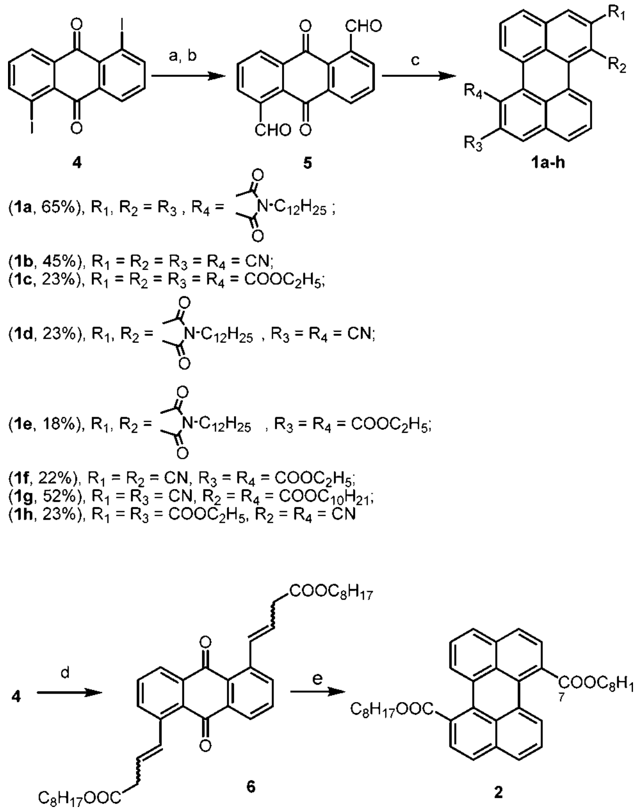
Scheme 1. Retrosynthetic Analysis



We recently reported a Wittig–Knoevenagel benzannulation strategy to synthesize acene diesters, dinitriles, and diimides.[11] Starting from aromatic *ortho*-dialdehydes, we performed Wittig olefination with 2-(triethyl-λ_5-phosphanylidene)-succinyl derivatives such as diesters, dinitriles, or imides. (The Wittig reagents were generated from the Michael addition of triethyl phosphine to electron-deficient alkenes.) With DBU as a basic catalyst, the intermediates can then undergo intramolecular Knoevenagel condensation to produce acene diester, dinitrile, or imide (Scheme 1). Because the perylene skeleton is composed of two naphthalene units, we can adopt this benzannulation reaction to make *Z*-shape perylenes. As depicted in Scheme 1, 9,10-anthraquinone-1,5-dicarbaldehyde should be the proper starting material for this purpose. After a double benzannulation reaction, Z-shape perylenes with electron-withdrawing substitutions at *ortho*-*bay* positions should be selectively produced.

The synthetic route to the target *Z*-shape tetrasubstituted perylenes (**1a**–**h**) is outlined in Scheme 2. The key building block 9,10-anthraquinone-1,5-dicarbaldehyde **5** was synthesized from 1,5-diiodo-9,10-anthraquinone **4**[12] after Heck coupling[13] (with styrene) and ozonolysis. The dicarbaldehyde **5** was then subjected to the Wittig–Knoevenagel benzannulation as described previously to furnish the *Z*-shape perylene diimide (**1a**), tetranitrile (**1b**), and tetraester (**1c**). It should be noted that the benzannulations proceed in respectable yields despite mixtures of *E*/*Z* isomers being produced in Wittig reactions. Such synthetic efficiency is acceptable considering four C–C bonds are formed in one reaction. Successive additions of different Wittig reagents during the benzannulation reactions can lead to hybrid perylenes with dissimilar substitutions at two sides of the molecules (**1d**, **1e**, and **1f**). Another class of hybrid perylenes (**1g** and **1h**) is centrally symmetric yet carries different substitutions at the 1 and 2 positions. Their synthesis can be accomplished by utilizing Wittig reagents generated by Michael addtion to (*E*)-alkyl 3-cyanoacrylate or alkylation of ethyl (triphenylphosphoranylidene)acetate (see Supporting Information). With a similar retrosynthesis and the identical starting compound, we can also synthesize dialkyl perylene-1,7-dicarboxylate **2** from precursor **6** (synthesized *via* Heck coupling as a mixture of olefin regioisomers) *via* a double Knoevenagel condensation.

Scheme 2. Synthesis of **1a**–**h** and **2**[a]



[a] Reagents and conditions: (a) Styrene, $(MeCN)_2PdCl_2$, Bu_4NBr, Et_3N, toluene, 100 °C, 24 h, 64%; (b) Ozone, CH_2Cl_2, $(CH_3)_2S$, −78 °C, 10 min, then to rt, 2 h, 78%; (c) PEt_3, A or B or C substrate (A = 1-Dodecyl-1*H*-pyrrole-2,5-dione; B = Fumaronitrile; C = Diethylmaleate), CH_2Cl_2, 0 °C to rt, 2 h, DBU, rt, 2 h; (d) Octylbut-3-enoate, $(MeCN)_2PdCl_2$, Bu_4NBr, Et_3N, 100 °C, 24 h, 59%; (e) NaO*t*Bu, *tert*-butanol, rt, 2 h, 26%.

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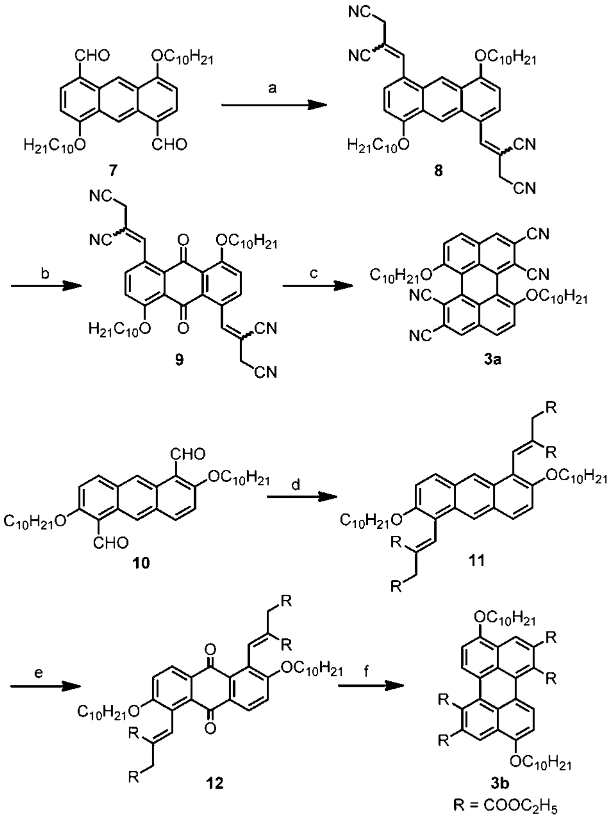
In Scheme 3, we describe a similar strategy to synthesize *Z*-shape perylene compounds with extra alkoxy substitutions at the *bay* and *peri* positions. Since the appropriately substituted diformyl anthraquinones are not readily accessible as **5**, we altered the synthetic sequence by performing the Wittig (or Wittig−Horner) reaction on dialkoxyl diformyl anthracene **7** and **10** (synthesized *via* Vilsmeier formylation)[14] to yield **8** and **11** respectively. The anthracene core was then oxidized with chromium oxide[15] to yield anthraquinone derivatives **9** and **12**. These two compounds were then subjected to Knoevenagel condensation in the presence of DBU to produce the desired perylene derivatives **3a** and **3b**.

A single crystal of **3a** suitable for crystallography analysis was grown from a saturated chloroform solution. As expected, the perylene skeleton of **3a** shows a significant twist near the *bay* area (Figure 1). The dihedral angle between two naphthyl units (25.16°) is evidently smaller than that of 1,6,7,12-tetrachloro PDI (36.7°),[16a] yet comparable to those of *bay* disubstituted derivatives such as Meador's Z-shape PDI (25°)[10] and 1,7-bis-perfluorobutyl PDI (28.9°).[16b] Such twisting effectively prevents intermolecular $\pi-\pi$ interactions. The closest intermolecular contact in the unit cell is between the perylene plane and decyloxy chain along the *b* axis (Supporting Information).

Scheme 3. Synthesis of **3a** and **3b**[a]



[a] Reagents and conitions: (a) PEt_3, fumaronitrile, CH_2Cl_2, 0 °C to rt, 3 h, 55%; (b) CrO_3, AcOH−H_2O, acetone, rt, 24 h, 52%; (c) DBU, CH_2Cl_2, rt, 3 h, 46%; (d) NaH, bis(2,2,2-trifluoroethyl) phosphite, diethylmaleate, THF, reflux, 24 h, 62%; (e) CrO_3, AcOH−H_2O, acetone, rt, 6 h, 81%; (f) DBU, toluene, reflux, 12 h, 71%.

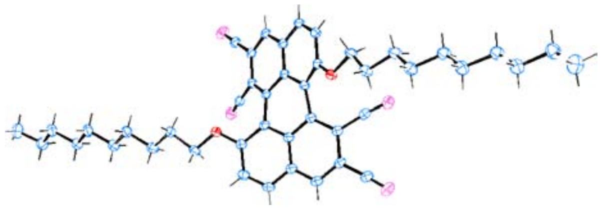


Figure 1. X-ray crystal structure of **3a**.

The frontier orbital energy levels of these *Z*-shape perylenes are probed by cyclic voltammetry, and the results are listed in Table 1. The first reductive wave of diimide **1a** (−0.99 eV) is very similar to that of its linear counterpart PDI (Table 1),[17] indicating little positional effect. However, a positional effect can manifest *via* steric interactions. For example, all ester groups in 3,4,9,10-perylene tetraester (PTE) must be orthogonal to the perylene plane to alleviate the 1,3-interaction. The resonance effect of the electron-withdrawing ester groups is weakened in this conformation; hence the reductive potential of PTE[18] is noticeably more negative than that of **1c**. The steric factor is also responsible for the discrepancy between **1g**'s and **1h**'s reductive potentials; when the bulkier ester group is placed at the *bay* position, the perylene skeleton is more twisted and therefore harder to reduce. Likewise, the dramatic elevation of the reductive potential from −0.65 eV for **1b** to −0.97 eV for **3a** should also be attributed to a similar skeletal twist. Predictably, electron-donating alkoxyl substituents lower the oxidative potential considerably (1.52 eV in **1c** to 1.07 eV in **3b**). Among the three types of functional groups, nitrile clearly exerts the strongest stabilization on the LUMO. The first reduction wave of tetranitrile **1b** is −0.64 eV, which is on par with many electron acceptors or N-type organic materials.

The photophysical data are also listed in Table 1. Selected absorption and emission spectra (**1a**−**c**, **2**, and **3a**) are shown in Figure 2. Both absorption and emission spectra of **1a** and **1c** are blue-shifted compared to *linear* counterparts like PDI and PTE. Because the LUMO levels of **1a** and **1c** are comparable or even lower than those of PDI and PTE, the hypsochromic shifts must be attributed to the suppression of HOMO levels by the *ortho* and *bay* substitutions. More surprisingly, absorption maxima of **1c**

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Table 1. Optical and Electrochemical Data

compd	λ_{max}/nm (log ε)[a]	λ_{max}/nm (Φ_{fl})[b]	E_{red}/V	E_{ox}/V
1a	482 (4.56)	500 (0.36)	−0.998	1.625
1b	457 (4.48)	475 (0.38)	−0.648	–
1c	429 (4.56)	486 (0.07)	−1.319	1.520
1d	468 (4.49)	487 (0.55)	−0.905	–
1e	463 (4.55)	497 (0.18)	−1.143	1.570
1f	451 (4.47)	504 (0.35)	−1.043	–
1g	433 (4.54)	486 (0.17)	−1.088	–
1h	459 (4.52)	480 (0.67)	−0.987	–
2	440 (4.43)	503 (0.24)	−1.335	1.326
3a	516 (4.48)	552 (0.83)	−0.974	1.472
3b	459 (4.50)	550 (0.54)	−1.487	1.067
PDI	523	536	−1.06	–
PTE	472	493	−1.50	–

[a] Measured in dichloromethane with a concentration of 1×10^{-5} M. [b] Determined using the integrating sphere method as described by de Mello et al.[19]

and **1g** exhibit slight hypsochromic shifts even to unsubstituted perylene (436 nm) and 1,7-diester **2** (440 nm). These results clearly indicate functionalization at the *ortho* position leads to hypsochromic shifts by suppressing the HOMO levels. This conclusion is well corroborated by other recently reported *ortho* substituted PDI derivatives.[9] Compounds with ester groups at *bay* positions (**1c**, **1e**, **1f**, **1g**, **2**) generally exhibit less structured emission spectra, lower fluorescence quantum yields, and larger Stokes shifts, all indicating rather flexible equilibrium structures.

In conclusion, we have synthesized *Z*-shape perylene systems *via* a Wittig–Knoevenagel benzannulation strategy. The photophysical and electrochemical properties of these compounds were studied. Some compounds with low LUMO energies are promising candidates for n-channel semiconductors. Since the reactive *peri* sites are unsubstituted in these perylenes, a wide range of further functionalization can be carried out, including the synthesis of push–pull perylenes, perylene-based electron acceptors, and higher rylenes.[20] All these challenges and opportunities are currently being exploited in our group.

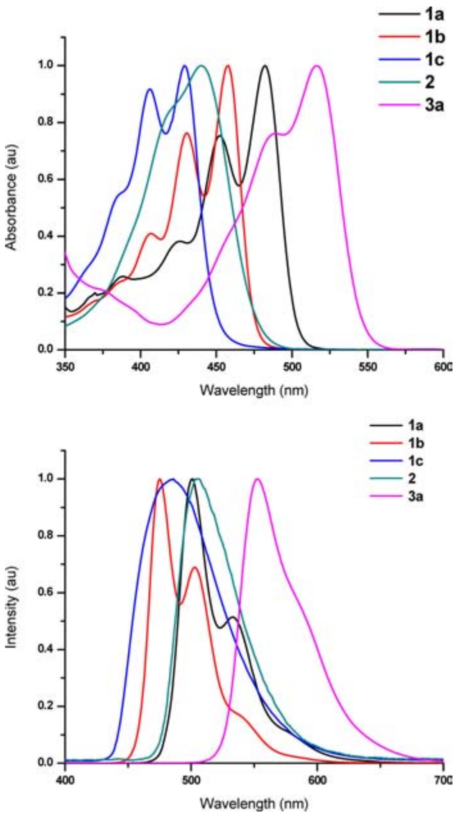

Figure 2. Normalized absorption and emission spectra of compounds **1a**–**c**, **2**, and **3a**.

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Supporting Information Available. Experimental details, spectral characterizations, X-ray, UV, CV graphs are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.