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Twisted, *Z-Shaped* Perylene Bisimide

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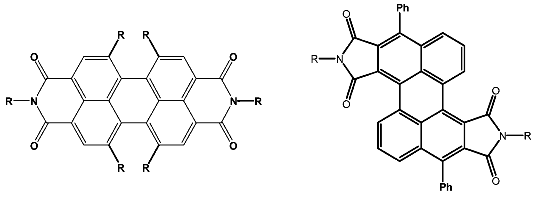
Perylene bisimides have found use in a wide range of applications, including electron-transfer systems,[1] liquid crystals[2] and other supramolecular assemblies,[3] photovoltaics,[4] and fluorescent sensors.[5] Interest in these compounds is due to their high fluorescence quantum yields and tunable absorption and emission properties. A diverse library of *linear* perylene bisimides (Figure 1) has been prepared from commercially available perylene anhydride or dianhydride and a wide array of amines via conventional imidization chemistry. Alkylamines or amine-terminated poly(ethylene glycol)s have been used to enhance solubility and/or impart liquid crystallinity. Approaches have also been reported to asymmetrically substituted bisimides[6] containing both a solubilizing group and an active unit, e.g. an electron donor or acceptor, to endow a specific function to the perylene. Significant attention has also been given to attaching pendant groups directly to the perylene core,[7] which can dramatically alter excited-state properties.



Linear Bisimide
R = generic group

Z-shaped Bisimide (**1**)
R = n-C_8H_{17}

Figure 1. *Linear* and *Z-shaped* perylene bisimides.

We are excited to report the first example of a nonlinear or *Z-shaped* perylene bisimide, **1**. This new bisimide differs from conventional *linear* systems in both the position and size of the imide rings. In addition, steric interactions between the imide carbonyls and hydrogens on C-6 and C-12 result in a twisting of the perylene ring system (vide infra). These changes, however, produce only minor electronic perturbations of the perylene bisimide **1**, and the favorable properties observed in *linear* systems, including visible absorption/emission and high fluorescence quantum yields, have been retained.

The synthesis of **1** employs a well-known photochemical reaction; the Diels−Alder trapping of *o*-methylphenyl ketone derived *o*-xylyenols (photoenols). Yang and Rivas first reported that cycloaddition of dimethyl acetylenedicarboxylate with *o*-xylyenol **3**, generated by photolysis of *o*-methylbenzophenone **2**, produced tetralin **4** in 65% yield (Figure 2).[8] This chemistry has been widely employed in the synthesis of fused six-membered ring systems.[8] Most of these applications have utilized ketone precursors capable of generating a single *o*-xylylenol.

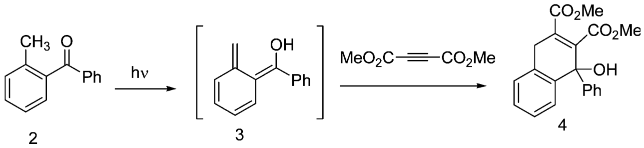
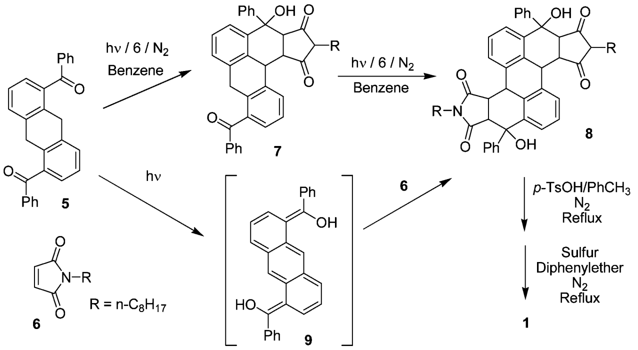


Figure 2. Diels−Alder trapping of *o*-xylyenol, **3**.

We have extended this chemistry to diketones, such as **5**, which are capable of generating two distinct *o*-xylylenols and have found that this powerful synthetic methodology offers a versatile, regiospecific, high-yield route to a variety of highly substituted anthracenes, phenanthrenes, and polymers.[9] We have now turned our attention to its use in the synthesis of novel polycyclic aromatic hydrocarbons, such as **1**.

Scheme 1. Synthesis of Perylene Bisimide Precursor, Bisadduct **8**



Thus, irradiation of **5** in the presence of 2.2 equiv of *N*-octylmaleimide **6** produced bisadduct **8** in 49% yield as a mixture of diastereomers (Scheme 1). While formation of bis-*o*-xylylenol intermediate **9** is possible, our work with related diketones suggests that the more likely pathway to bisadduct **8** involves enolization of **5** and trapping to form monoadduct **7** followed by a second enolization/trapping sequence.[10] Subsequent dehydration and aromatization gave *N*,*N′*-bis(octyl)-3,9-diphenylperylene-1,2,7,8-tetracarboxyl bisimide **1** as an orange solid in 18% overall yield from **5**.

Z-shaped perylene bisimide **1** is soluble in polar organic solvents. Room-temperature absorption and emission spectra of **1** are shown in Figure 3. Compound **1** has an absorption λ_{max} near 491 nm with an extinction coefficient of 29,000 $M^{-1}cm^{-1}$.[11] Fluorescence of **1** exhibits a Stokes' shift of 26 nm ($\lambda_{max} = 517$ nm) and a quantum yield of 0.67.[11] Intense green emission is observed both in solution and polystyrene films (inset of Figure 3). Emission from **1** does not exhibit solvatochromism. Room-temperature fluorescence decay measurements in CH_2Cl_2 revealed a single-exponential lifetime of 5.01 ns, consistent with a singlet excited state. Solid-state emission is bright orange, indicative of exciplex formation. Cyclic voltammetry on **1** in CH_2Cl_2, using a silver wire quasi-reference electrode

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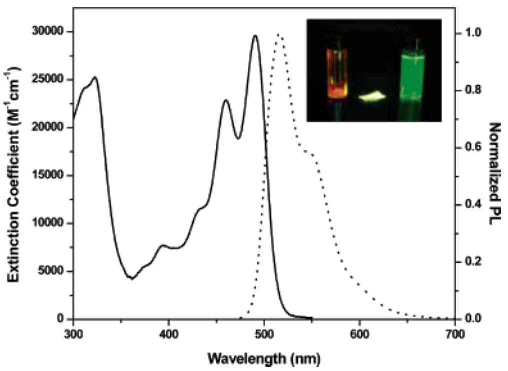

Figure 3. Absorption (solid line) and normalized emission (425 nm excit) spectra (dotted line) of **1** in CH_2Cl_2. (Inset): Emission from **1** in a pure microcrystalline sample (left), in a polystyrene film (center), and in CH_2-Cl_2 solution (right) excited with a hand-held, broadband UV source.

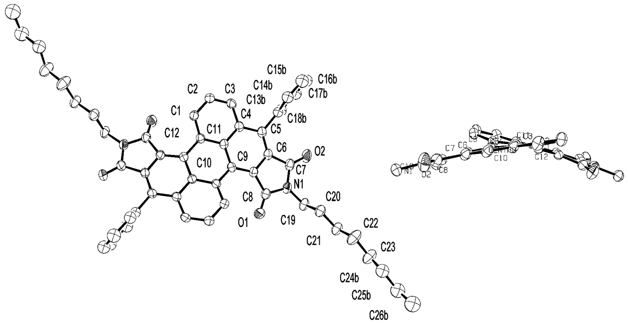

Figure 4. ORTEP (50% probability) of **1**. (Left) Top view. (Right) Side view (pendant groups have been removed for clarity).

and ferrocene as an internal potential marker, reveals two reversible[12] reduction potentials at −1.08 and −1.30 V, ca. 600 mV lower than similar *linear* bisimides.[1d]

X-ray crystallographic analysis of single crystals of **1**, grown from slow evaporation of benzene, revealed a substantial twist (19.5°) in the perylene core between each naphthyl unit (Figure 4).[13] This is not unexpected, as previous reports have shown that highly substituted perylenes are twisted, whereas unstrained derivatives are essentially flat.[14] Steric crowding in **1** also results in elongation (1.474(3) Å) of the C−C bonds connecting the naphthyl units, indicating development of single-bond character and loss of aromaticity. These data are consistent with the observed slight blue-shift in the absorption and emission spectra of **1** relative to those of the less crowded *linear* perylene bisimides. The unit cell of **1** consists of columnar structures of perylenes alternating with *n*-octyl chains from the perylene bisimide on an adjacent column. The observation of excimer emission from crystalline **1** is somewhat surprising given the large distance (8.2 Å with intercalated aliphatic chains) between perylenes in these columns.

We have reported the first synthesis of a *Z-shaped* perylene bisimide. As a key step, the Diels−Alder trapping of photochemically generated *o*-xylylenols was utilized. This versatile chemistry will enable the preparation of an array of new perylene bisimides with various functionalities on the imide rings and pendant phenyl groups. Despite the twisting of the perylene core, perylene bisimide **1** displays absorption and emission behavior similar to that of conventional *linear* perylene bisimides. These new bisimides should have a broad range of applications including electron transfer systems, molecular sensors and electronics, and liquid crystalline materials. We are currently exploring these avenues.

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Note Added after ASAP Publication. After this paper was published ASAP on December 23, 2005, the Scheme 1 title was corrected. The corrected version was published ASAP January 6, 2006.

Supporting Information Available: Synthetic and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Although conformational disorder present in the pendant octyl and phenyl groups, the perylene core is well defined. **4**: monoclinic, C_2/c, a = 22.0080(12) Å, b = 8.2920 (5) Å, c = 22.3830(12) Å, β = 93.089(1)°. Final R indices $[I > 2\sigma(I)]$ R1 = 0.0583, wR2 = 0.1502.

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