The synthesis of azaperylene-9,10-dicarboximides

Trisha L. Andrew, Brett VanVeller, Timothy M. Swager*

Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge MA 02139 (USA)

Fax: (+1) 617-253-7929

E-mail: tswager@mit.edu

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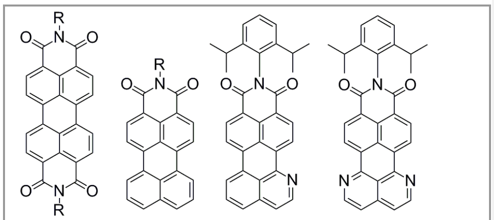
Abstract: The syntheses of two azaperylene 9,10-dicarboximides are presented. 1-Aza- and 1,6-diazaperylene 9,10-dicarboximides containing a 2,6-diisopropylphenyl substituent at the *N*-imide position were synthesized in two steps starting from naphthalene and isoquinoline derivatives.

Key words: perylenes, isoquinolines, cross-coupling, cyclization, oxidation

Boasting brilliant colors, large extinction coefficients, near-unity fluorescence quantum yields and remarkable photostability, perylene-based chromophores have found unique prominence as dyes and pigments.[1] Particularly, perylene-3,4,9,10-tetracarboxdiimides (PDIs, **1**) are suitable for demanding applications, such as photovoltaic devices,[2] dye lasers,[3] light-emitting diodes[4] and molecular switches.[5] The related perylene-3,4-dicarboximides (PIs, **2**) can be monofunctionalized more readily than **1**,[6] which is interesting for certain applications, such as fluorescence labeling and controlled conjugation to other fluorophores.

Although most of the aforementioned applications capitalize on the high fluorescence efficiencies of **1** and **2**, access to the PDI or PI triplet state represents a desirable goal for some niche applications, such as solar energy conversion,[7] and as a method to generate deep red and/or near IR phosphorescence. Previous attempts to directly attach late transition metals to the perylene skeleton resulted in minimal electronic interaction between the metal center and PDI π-system.[8] Moreover, it was found that introducing conjugated spacers between the metal center and PDI π-system only yielded non-emissive complexes.[7] Inspired by the superior photophysical properties and high phosphorescence quantum yields of cyclometalated platinum (II), and ruthenium (II) iridium (III) complexes,[9] we sought to synthesize PDI or PI analogs that contained a 2-phenylpyridine moiety that would eventually allow access to cyclometalated perylene complexes.

Along these lines, 1-azaperylene was previously synthesized and reported to undergo directed C-H activation to yield bay-functionalized 12-hydroxy-1-azaperylene, which displayed excited state intramolecular proton transfer (ESIPT).[10] However, due to the lack of notable functional groups in the perylene skeleton, a harsh anion-radical cyclization of either 1- or 8-(α-naphthyl)-isoquinoline was necessary to generate the 1-azaperylene chromophore. Moreover, we anticipated that the rigidity of 1-azaperylene, combined with its lack of solubilizing groups, would lead to complexes of poor solubility. Instead, we envisioned that (a) introduction of an electron- withdrawing imide moiety to the azaperylene skeleton would allow the use of a comparatively-mild, base-promoted cyclization procedure[11,12] to synthesize the desired azaperylene imides and that (b) introduction of bulky substituents at the *N*-imide position would greatly improve the solubility of the chromophore. Additionally, the resulting azaperylene imide chromophore would have bathochromically shifted absorption and emission spectra relative to the cyan-emitting 1-azaperylene.



1 **2** **3** **4**

Figure 1 Structures of PDI, PI and azaperylene imides

Initially, a one-step synthesis of 1-azaperylene-9,10-dicarboximide (**3**) by base-promoted heterocoupling of naphthalene-1,8-dicarboximide and 1-chloroisoquinoline was attempted, based on the previously-reported one-pot synthesis of terrylene diimides.[12] However, only homocoupling between naphthalene-1,8-dicarboximide reactants was observed and *N,N'*-bis(2,6-diisopropylphenyl) PDI was isolated in 80% yield. Therefore, a multi-step approach to **3** and **4** was pursued. Precursors **7**, **8** and **9** were synthesized by a one-pot Suzuki-Miyaura cross-coupling between a 4-bromonaphthalene-1,8-dicarboximide[13] and either an isoquinoline derivative[14] or a 2,7-naphthyridine derivative.[15] The boronic ester derivative of bromide **5** was generated in situ by standard palladium-catalyzed reaction with bis(pinacolato)diboron. Subsequent addition of the corresponding isoquinoline or 2,7-naphthyridine coupling partner furnished precursors **7**, **8** and **10** in good to high yield. The use of S-Phos was necessary in the cross-coupling reactions involving 1-chloroisoquioline and 1-chloro-2,7-naphthyridine (**9**), as other phosphine ligands afforded low product yields and resulted in extensive protodehalogenation.

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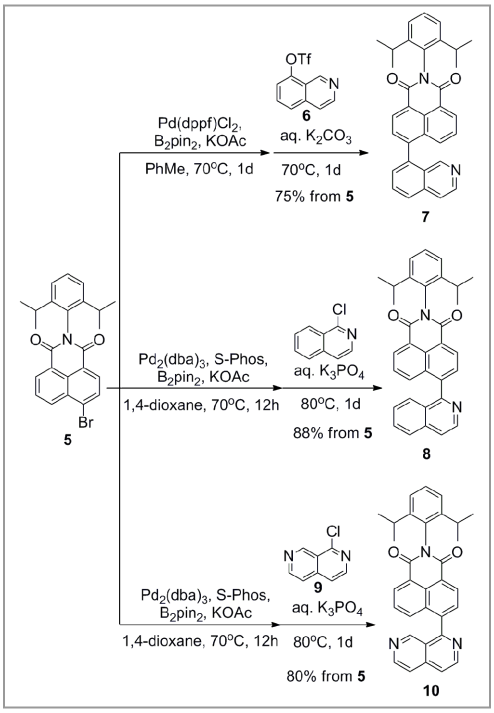
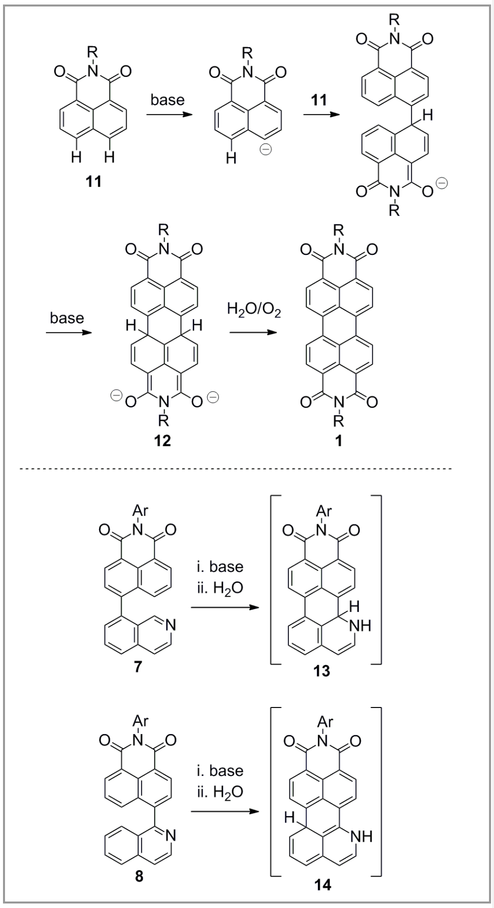


Scheme 1 Synthesis of precursors **7**, **8** and **10**.

In order to cyclize **7**, **8** and **10**, the base-promoted cyclization procedures described in the syntheses of extended rylene diimide chromophores were investigated.[11,12] In these examples, it is thought that nucleophilic attack of an arylide anion initially generates the leuco form of the chromophore (**12**), which subsequently oxidizes to form the rylene skeleton (Scheme 2).[16] Compounds **7** and **8**, which are both precursors to azaperylene imide **3**, differ only in the position at which the naphthalene imide and isoquinoline rings are linked. We anticipated (a) that these isomeric structures would display different amenabilities to the initial arylide attack and (b) that the resulting isomeric leuco forms of **3** would display varying stabilities to oxidation.

Treatment of **7**, **8**, and **10** with K_2CO_3/ethanolamine and subsequent heating initially resulted in the formation of the reduced versions of the desired azaperylene imide chromophores, which upon workup and oxidation formed the desired products (Scheme 3). The individual reduced forms of **3** and **4** generally displayed a greater resistance to oxidation relative to their all-carbon perylene analogs. For the base-promoted cyclization reactions of **7** and **10**, stirring under air after a water workup yielded **3** and **4**, respectively, after approximately 1 hour. In the case of precursor **8**, however, the yield of **3** was improved if the workup procedure included hydrogen peroxide. Based on this observation, we posit that leuco compound **14** is slightly more stable compared to leuco compound **13**. Unfortunately, attempts to isolate and purify the various reduced forms of **3** and **4** were unsuccessful, as the azaperylene imides were inevitably obtained in most trials.



Scheme 2 Base-promoted cyclization of rylene imides.

Azaperylene imide **3** was very soluble in CH_2Cl_2, $CHCl_3$, MeOH, EtOH and MeCN while **4** was very soluble in MeOH and MeCN and only partially soluble in $CHCl_2$ and $CHCl_3$. The absorption and emission spectra of **3** and **4** are shown in Figure 2. Both azaperylene imides display similar absorption and emission bands to the carbon analog **2** (R = 2,6-diisopropylphenyl). The fluorescence quantum yield is 93% for both **3** and **4**, compared to ca. 98% for **2**. Additionally, the fluorescence lifetimes of all three chromophores were also similar: 4.71 ns for **2**, 4.82 ns for **3**, and 4.94 ns for **4**.

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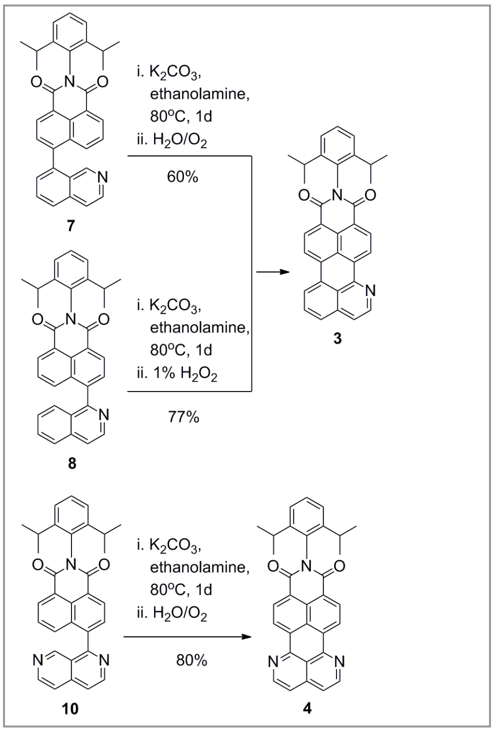

Scheme 3 Base-promoted cyclization to synthesize **3** and **4**.

In conclusion, azaperylene imide and diazaperylene imide were synthesized in two steps starting from naphthalene imide and either an isoquinoline derivative or a 2,7-naphthyridine derivative. Base promoted cyclization of binaphthoid intermediates resulted in reduced versions of the desired chromophores, which had a finite lifetime and could be oxidized to yield 1-aza- and 1,6-diaza perylene-9,10-dicarboximides. The azaperylene imides display similar photophysical characteristics to their carbon analogs. Studies into the cyclometalation of these chromophores are currently underway.

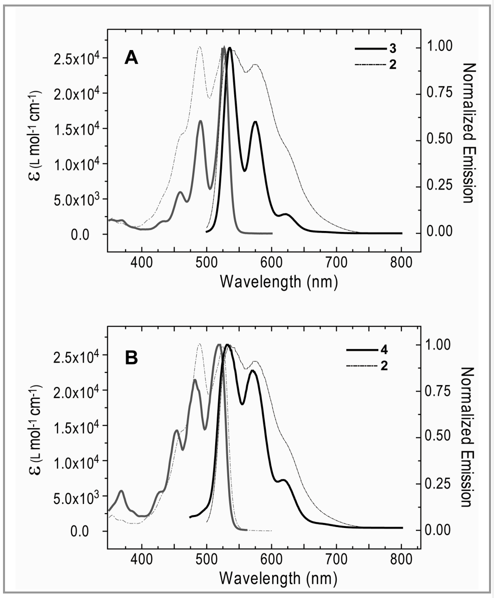

Figure 2 Absorption (grey) and emission (black) spectra of (A) **3** and (B) **4** in chloroform. The absorption and emission spectra of the carbon analog **2** (R = 2,6-diisopropylphenyl) is also superimposed (dotted line).

Supporting Information for this article is available online at http://www.thieme-connect.de/ejournals/toc/synlett.

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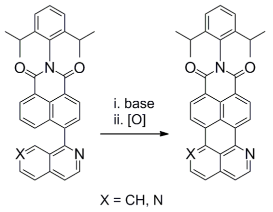

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