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Modular synthesis of asymmetric rylene derivatives†

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The modular synthesis of asymmetric rylenes from naphthalic anhydride derivatives is presented. Imidization, Suzuki–Miyaura coupling and cyclodehydrogenation reactions are utilized for the generation of novel functional rylenes with these three core transformations providing significant flexibility over the final structure. The combination of simple purification and high yields enables access to asymmetric rylenes with functional handles at the imide-position and site-specific incorporation of bay position substituents. The resulting library of perylenes and bisnapthalimide-anthracene derivatives showcase the presented methodology and the ability to tune optoelectronic and electrochemical properties.

Introduction

Rylenes encompass a large family of molecules that are comprised of naphthalene units joined at the *peri*-position,[1] including well-known and sought-after perylene diimides (PDIs). PDIs were originally used as dyes due to their high molar absorptivity and excellent chemical, thermal, light, and air stability.[2] More recently, other attractive properties of PDIs have emerged, such as high fluorescence quantum yield[3] and strong electron accepting (n-type) character,[4] lending to applications in fluorescent light collectors,[5,6] dye lasers,[7–9] electrophotography,[10] organic field-effect transistors,[11–13] and organic photovoltaics.[12,14] In particular, asymmetric substitution at the imide position has resulted in improved solubility and functionality, granting access to multichromophoric systems,[15,16] supramolecular architectures,[17] and incorporation into polymers for organic electronic applications.[18–20]

While asymmetric PDIs are attractive, their synthesis has proven challenging. In contrast to their symmetric counterparts, which are produced readily through the condensation of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) with aliphatic primary amines or anilines,[21] asymmetric PDIs are not typically accessible through direct imidization given the increased reactivity of the singly substituted monoimide species.[22] Instead, the typical approach involves an inefficient (<30% overall yield) stepwise synthesis; imidization of PTCDA with one amine, partial hydrolysis to the monoanhydride monoimide, and imidization with a second amine.[23–25] A one-step synthesis of asymmetric PDIs in ~40% yield was recently developed in our group by taking advantage of the difference in reactivity between alkyl- and aryl-amines, however the scope of products is limited to alkyl/aryl combinations.[26]

In seeking to further expand the availability and structural diversity of asymmetric perylenes, we report a modular approach to a wider range of functional asymmetric rylene derivatives. This strategy is enabled by the disconnection of the perylene/rylene core to give the readily available naphthalic anhydride starting material (Fig. 1). By having a common initial building block (substituted naphthalimide – one half of PDI), the functionalization and purification is greatly simplified. As a result, high yielding imidization, followed by Suzuki–Miyaura coupling and cyclodehydrogenation reactions could be utilized to achieve the asymmetric PDI targets in greater than 40% yield.

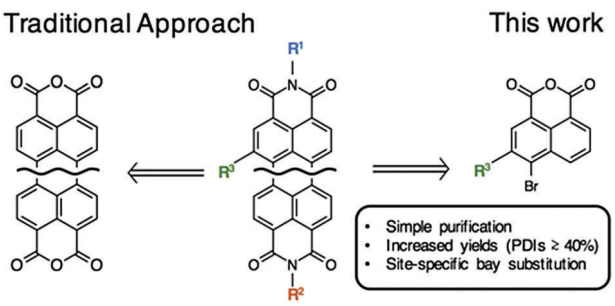

Fig. 1 Retro-synthetic comparison of asymmetric rylenes through the traditional approach starting from PTCDA *versus* the presented methodology from naphthalic anhydride derivatives.

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Moreover, the synthesis could be extended to bay-substituted PDIs as well as larger-core rylenes, highlighting the versatility of this modular approach.

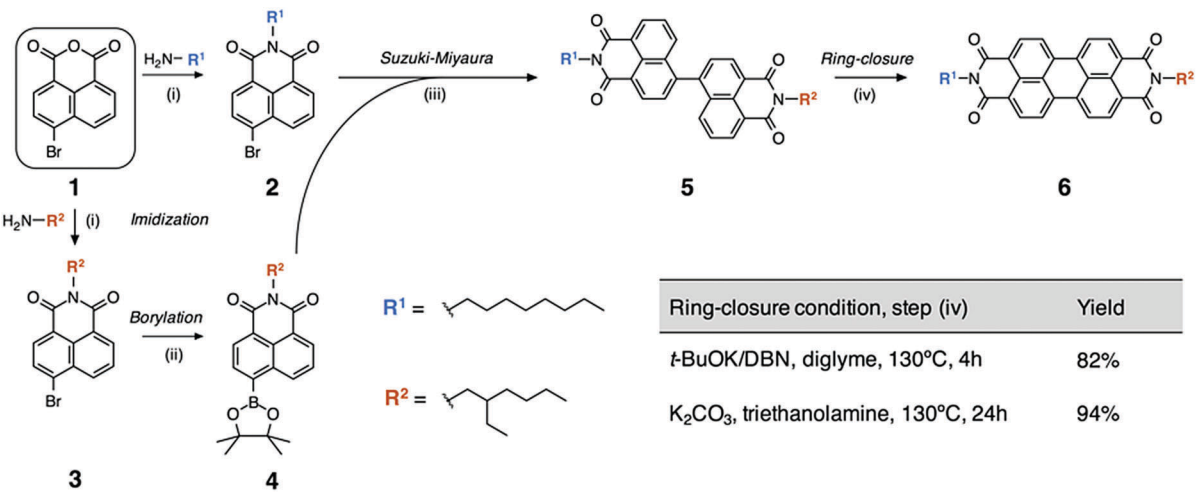
Results and discussion

The general synthetic protocol to asymmetric PDIs is represented in Scheme 1. Bromination of the inexpensive ($\sim$\$50 kg^{-1}) commercial reagent "naphthalic", to produce 4-bromo-1,8-naphthalic anhydride (**1**), followed by imidization, is easily achieved by reacting with the desired primary amine in ethanol (EtOH) at reflux. The reaction mixture changes from an opaque to translucent solution after 2 hours due to improved solubility as **1** is converted to the imides, for example 4-bromo-1,8-naphthalimide **2** (*n*-octyl) and **3** (2-ethylhexyl) in near quantitative yields. The robust nature of this process allows for facile reaction monitoring and product purification. Following imide diversification, Miyaura borylation of **3** then leads to the boronic ester naphthalimide **4**, which could be cross coupled by Suzuki–Miyaura cross-coupling with a different bromo-naphthalimide **2** derived from the same bromo-substituted starting material, **1**. This results in clean conversion to the desired asymmetric product (**5**), which is easily purified through standard techniques. A base catalyzed cyclodehydrogenation ring-closure of **5** was then investigated for formation of the asymmetric PDI **6**. Initial cyclodehydrogenation attempts employed potassium *tert*-butoxide (*t*-BuOK) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in diglyme,[27] however the reaction provided inconsistent yields. As an alternative, potassium carbonate (K_2CO_3) in ethanolamine at elevated temperature (130 °C) was investigated for cyclization, but this procedure leads to transimidation of less sterically hindered side-chains (*e.g.*, *n*-alkyl) by ethanolamine (Fig. S1, ESI†).[28] Triethanolamine was selected as an alternative to ethanolamine,[29] and the change from primary amine to tertiary amine was found to mitigate transimidation, while providing excellent yields ($\sim$94%).

The conversion from **5** to **6** can be monitored using proton NMR (Fig. 2a), particularly in the aromatic region as the five peaks of the Suzuki-coupled diad (**5**) collapse to two doublets (**6**) with formation of the perylene core. Additionally, the success of the ring-closing can also be observed by eye due to the substantial bathochromic shift in absorbance ($\sim$150 nm) from **5** (yellow solution) to **6** (bright red solution), shown as an inset in Fig. 2b.

To highlight the versatility of the aforementioned methodology a library of functional asymmetric PDIs were synthesized, as shown in Table 1. Given the modular nature of this strategy side chains can be easily mixed and matched, for example, partnering naphthalimide **4** containing a solubilizing 2-ethylhexyl chain with functional naphthalimides bearing a carboxylic acid or alkene chain to give asymmetric PDIs **7** and **8** respectively. Moreover, two orthogonal functionalities, such as a carboxylic acid and alkene can be easily paired with this approach to give **9**. Overall, the yields range from 41% to 51%, as compared to <30% for traditional methods.

While varying imide substituents on PDIs is a facile route to increase solubility and incorporate functional handles, modifications at the **1**, **6**, **7**, and **12** (bay) positions on the perylene core directly influence the optoelectronic properties of the molecule.[30] As with direct imide substitutions towards asymmetric PDIs, reactions at the perylene core typically produce mixtures of mono-, di-, tri-, and tetra-substitution that are challenging to separate, reducing reaction yields and leading to impure samples.[30] The power of this modular strategy is that by constructing the central perylene core in a step-wise fashion starting from discrete naphthalic units, precise control over the location of the bay substitution in the final PDI is possible. As shown in Fig. 3a, functional naphthalic anhydrides are commercially available, which provides easy access to alkoxy-functional naphthalimides, such as methoxy-substituted naphthalimide (**10**), through Williamson-ether synthesis (Fig. 3a). Suzuki–Miyaura coupling of **10** with a boronic ester naphthalimide (**11**), bearing no bay-substituents and a functional (alkene) imide chain,



Ring-closure condition, step (iv)	Yield
t-BuOK/DBN, diglyme, 130°C, 4h	82%
K_2CO_3, triethanolamine, 130°C, 24h	94%

Scheme 1 Representative synthesis of asymmetric PDI 1. (i) EtOH, reflux, 4 h, 87% (**2**) and 85% (**3**); (ii) Pd(dppf)Cl_2, bis(pinacolato)diboron, KOAc, *p*-dioxane, 100 °C, 24 h, $\sim$quantitative; (iii) K_2CO_3 (aq.), Pd(PPh_3)$_4$, toluene, 100 °C, 12 h, 67%; (iv) K_2CO_3, triethanolamine, 130 °C, 24 h, 94%. Comparison between reaction yields for two ring-closure conditions is provided as an inset.

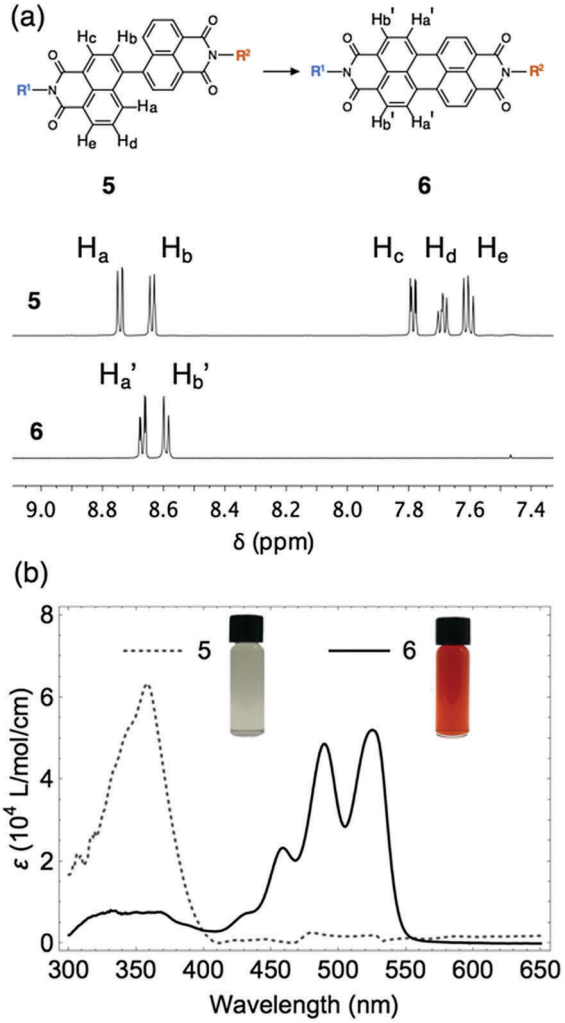
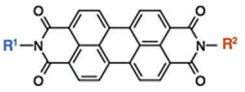


Fig. 2 Monitoring of ring-closure reaction to convert **5** to **6**. (a) Structures with corresponding ^{1}H-NMR, showing diagnostic aromatic protons. (b) Absorption spectra (100 μM in dichloromethane) and corresponding images of **5** and **6** (5 mM in dichloromethane).

produces a PDI that is asymmetric at both the imide and bay positions (**12**). It was immediately apparent that methoxy substitution altered the electronic properties of the perylene core, given the visual difference in color for solutions of **12** (pink) relative to non-bay substituted PDIs (**6–9**, red) (Fig. 3b). UV-Vis absorption spectroscopy quantified this observation, revealing a 30 nm bathochromic shift for methoxy-substituted PDI (**12**) relative to unsubstituted PDI (**6**) (Fig. 3b). Additionally, cyclic voltammetry (CV) measurements show that bay substitution with an electron-donating methoxy group leads to an increase in reduction potentials for **12** (−1.19 and −1.50 V) relative to **6** (−1.11 and −1.41 V) (Fig. S2, ESI†), providing further evidence that bay substitution can be used to directly tune the electronic properties of PDIs.

As a final demonstration of modularity of this approach a novel core-extended rylene derivative was synthesized based on a structure inspired by pentarylene[30] and an aminoanthraquinone-based rylene.[31] As shown in Fig. 4a, the reaction of two

Table 1 Asymmetric PDIs (**6–9**) synthesized with varying imide substituents. Overall yields account for all synthetic steps



Entry	R^1	R^2	Overall yield (%)
6			51
7			44
8			42
9			41

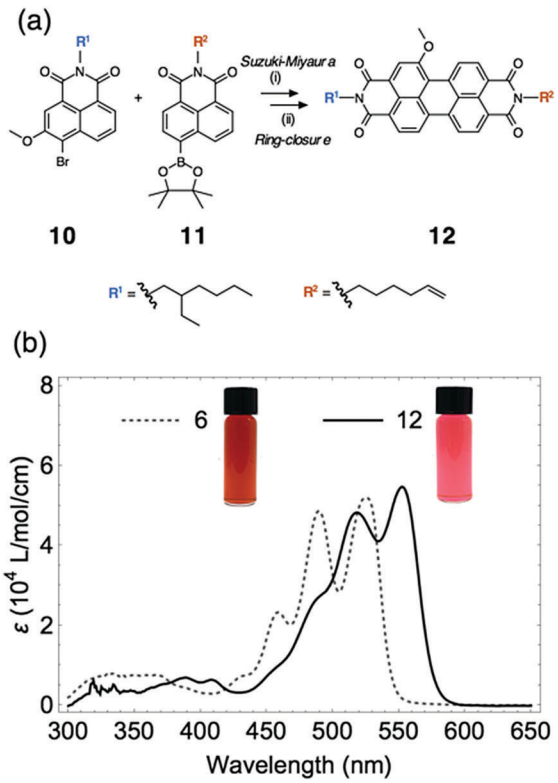


Fig. 3 (a) Representative synthesis of bay-substituted PDI **12**. (i) $K_2CO_{3(aq)}$, $Pd(PPh_3)_4$, toluene, 100 °C, 12 h, 63%; (ii) K_2CO_3, triethanolamine, 130 °C, 20 h, 91%. (b) Absorption spectra (100 μM in dichloromethane) and corresponding images of **6** and **12** (5 mM in dichloromethane).

equivalents of borylated naphthalimide (**13**) with 1,5-dibromoanthracene (**14**) produces a dinaphthalimide-anthracene triad (**15**). In contrast to the synthesis of electron deficient cores, such as perylene, a two-step ring-closure is required for the

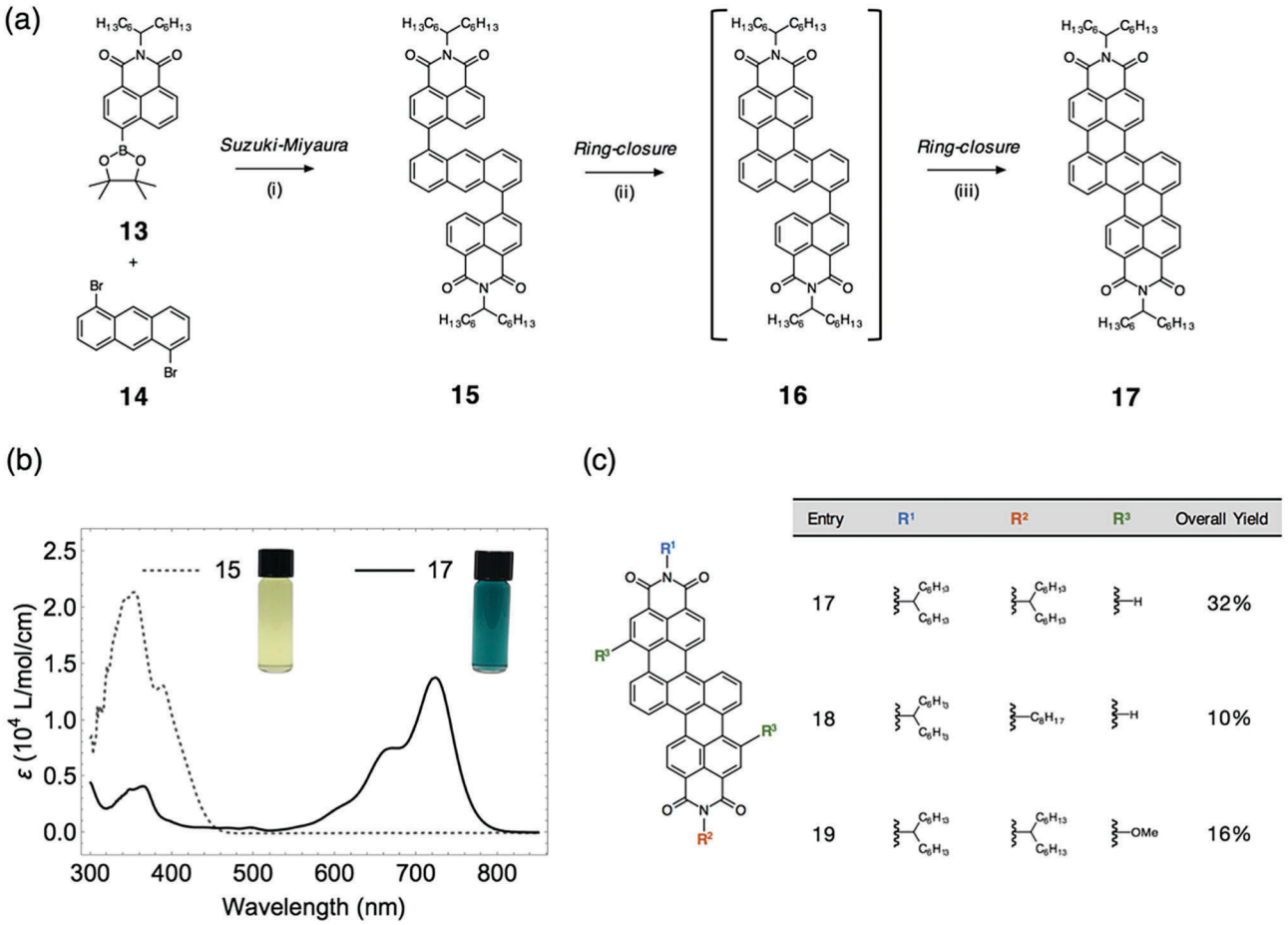


Fig. 4 Core-extended rylenes, synthesis and absorption. (a) Representative synthesis of **17**; (i) $K_2CO_{3(aq)}$, $Pd(PPh_3)_4$, toluene, 100 °C, 12 h, 68%; (ii) $FeCl_3$, nitromethane, DCM, 55 °C, 24 h; (iii) K_2CO_3, ethanolamine, 130 °C, 16 h, 56%. (b) Absorption spectra of **15** and **17** (100 μM in dichloromethane) and corresponding images of solutions in vials (5 mM in dichloromethane). (c) Summary of core-extended rylene derivatives (**18–20**) synthesized with varying imide and bay substituents.

anthracene-based derivative due to the greater electron density and corresponding lower acidity of the aromatic protons.[32] The first ring closure was accomplished using traditional Lewis-acid chemistry with iron(III) chloride to give the partially closed derivative, **16**, which was used directly for the second ring closing step. Employing different conditions (K_2CO_3 in ethanolamine or triethanolamine), then gives the final rylene product (**17**). The dual ring-closures results in a dramatic bathochromic shift in absorption (370 nm) on going from the precursor **15** to rylene **17** (Fig. 4b) with the distinct change in color, from yellow (**15**) to green-blue (**17**), being indicative of successful ring-closing. Additionally, UV-Vis absorption spectroscopy reveals an absorption maximum in the near infrared region (λ_{max} = 723 nm) for **17**, highlighting its narrow energy-gap, which falls between terrylene diimide and quatterylene dimide derivatives, demonstrating the ability to significantly tune the electronic structure through the introduction of a π-extended core.[33] The synthesis of asymmetric extended-core rylenes was achieved in a similar fashion to that described in Fig. 4a, however using a stepwise Suzuki–Miyaura coupling. In short, coupling compounds **13** with **14** in a 1 : 1 molar ratio produces a diad (**S1**), which is subsequently coupled with the borylated derivative of naphthalimide **2** to yield an asymmetric triad (**S2**) (chemical structures given in Chart S1, ESI†). Cyclodehydrogenative ring-closing of the triad provides an asymmetric extended rylene derivative (**18**), highlighting the ability to incorporate different side chains at the imide positions for classes of larger rylenes beyond PDIs using this methodology. Moreover, the electronic properties of the higher order rylene can be tuned with core substitutions, which was demonstrated for methoxy-substituted rylene **19**, synthesized in an analogous fashion to **17**. As observed for PDIs, methoxy substitution of extended rylenes in the bay position led to a bathochromic shift (~20 nm) in absorption, which corresponds with a noticeable color change in solution, going from **17** (blue-green) to **19** (green) (Fig. S3, ESI†). Additionally, CV showed a similar increase in reduction potentials from −0.67 and −0.86 V to −0.79 and −0.96 V for **17** and **19** respectively (Fig. S4, ESI†). The asymmetric and bay-substituted core-extended rylenes showcase the modularity of this approach.

In summary, we have developed a strategy for the facile synthesis of asymmetric PDIs that takes advantage of modular naphthalimide units to provide increased versatility, greater

atom efficiency, and simpler purification. Using cross-coupling and base-catalyzed ring-closing, asymmetric PDIs and extended rylene derivatives can be prepared in high yields with a variety of substituents in both the imide and bay positions. This methodology provides an efficient avenue towards a wide range of novel, tunable, and functional rylene structures for utility in electronic materials applications.

Competing financial interest

The authors declare no competing financial interest.

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