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Graphical Abstract

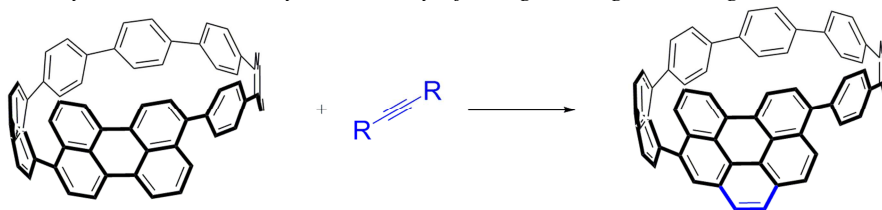
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ABSTRACT

We have synthesized a cycloparaphenylene containing a perylene motif that is a model for a carbon nanotube sidewall. The reactivity of the sidewall model towards a Diels-Alder reaction using a masked acetylene was examined and similar reactivity was observed between the macrocyclic and planar substrate. This study suggests that a Diels-Alder reaction is a viable method for carbon nanotube growth using an appropriate template.

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1. Introduction

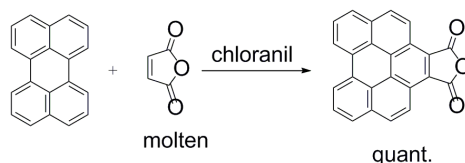
Carbon nanotubes (CNTs) have unique optoelectronic properties that are highly dependent on the chiral index (i.e. structure and diameter) of the CNT.¹ Although promising as a new material, current CNT synthesis is hampered by a lack of structural control. Currently no scalable method exists to produce homogenous CNTs with a predefined chiral index.² A promising approach towards overcoming this challenge is to utilize a template for growing CNTs that would predefine the chirality and diameter of the resultant nanotube.³ One proposed strategy to grow CNTs from a template is to utilize a Diels-Alder cycloaddition with acetylene or an acetylene equivalent as a carbon feedstock on an extended cycloparaphenylene template. This is an attractive method since no new nanotubes are created under Diels-Alder conditions and CNTs can only be elongated from existing templates with predefined diameter and chirality. In the reaction, an acetylene dieneophile would undergo [4+2] cycloaddition with the diene bay region of the template to form a new 6-membered ring, followed by rapid extrusion of H₂ to regain aromaticity.⁴ (Figure 1) Continuing this process on an adjacent bay region would subsequently form another new bay region and this process can continue indefinitely, sequentially

creating a new bay region with each cycloaddition.

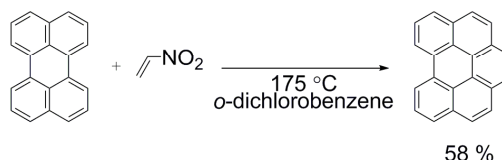
In principle, a small hydrocarbon template should provide the necessary architecture for dictating the diameter and chirality for growing a CNT using a cycloaddition reaction. The simplest

Previous work

a. Clar



b. Scott



This Work

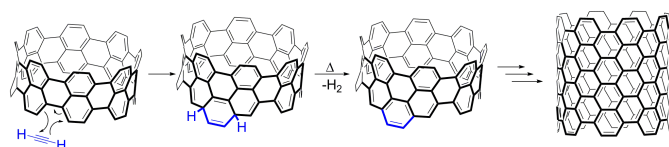
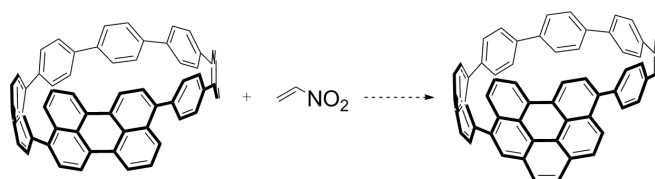
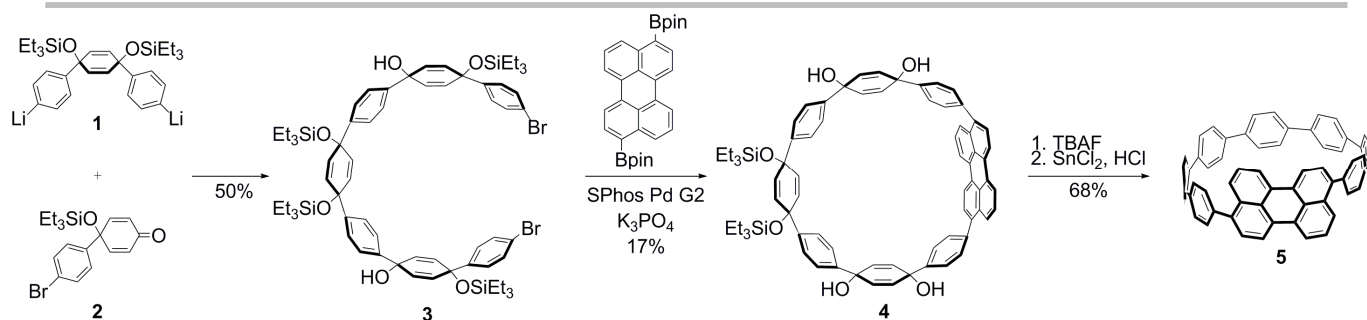


Figure 1: A proposed method for growing CNTs using a Diels-Alder reaction

Figure 2: a: Early work from Clar b: Scott's system using nitroethene c. Diels-Alder on perylene in a macrocyclic system



Scheme 1: Synthesis of a model CNT sidewall (**5**)

model for this system would be biphenyl which upon cycloaddition and rearomatization would yield phenanthrene. Unfortunately, no known Diels-Alder reaction exists on biphenyl likely due to the high loss of aromatic stabilization energy that accompanies cycloaddition. Although biphenyl is unreactive under Diels-Alder conditions, previous work from Scott⁴ and Clar⁵ showed that cycloaddition and rearomatization was indeed possible on larger polycyclic aromatic hydrocarbon (PAH) systems. The Diels-Alder reaction on a bay region of a PAH was first shown on perylene by Clar⁵ using maleic anhydride and chloranil as an oxidant (Figure 2a). More recently Scott⁴ has shown that a variety of dieneophiles, including nitroethylene^{4c} undergo cycloaddition with perylene and subsequent loss of HONO and H₂ re-aromatizes the ring forming benzannulated perylene (Figure 2b). While extensive work has been conducted with flat perylene or bisanthrene derivatives to study the reactivity in the bay region for cycloaddition, no work has experimentally^{4b,6} examined a [4+2] cycloaddition in a macrocyclic cycloparaphenylene⁷ system that would serve a model for nanotube growth. Herein, we report our efforts at synthesizing cyclo(3,9)-perylenehepta(paraphenylene) (**5**) a CPP containing a perylene fragment embedded in the macrocycle, as well as the viability of this model to undergo a Diels-Alder reaction with nitroethylene for benzannulation.

2. Results and discussion

To experimentally investigate a Diels-Alder reaction on a model CNT sidewall we envisioned synthesizing a cycloparaphenylene (CPP) macrocycle containing a perylene subunit. The synthetic strategy utilized methodology similar to our previous syntheses of CPPs with cyclohexadiene units acting as masked benzene rings.⁸ To incorporate perylene into a CPP we envisioned a synthetic plan outlined in Scheme 1 where functionalized perylene is incorporated in a late stage Suzuki-Miyaura macrocyclization reaction. Dibromide **3** can be accessed from precursor **1** through double lithiation and nucleophilic addition to ketone **2**. Functionalized perylene was synthesized through bromination of perylene to afford a mixture of 3,10 and 3,9 dibromoperylene⁹ and we found that repeated recrystallization in 5/3 aniline/toluene afforded enriched 3,9-dibromoperylene in a ratio of 16:1. Subsequent Miyaura borylation of 3,9-dibromoperylene afforded the desired bis-boronate coupling partner and the structure was unambiguously confirmed by X-ray crystallographic analysis as the substituted 3,9-perylene. Suzuki-Miyaura cross coupling using Buchwald's second generation SPhos precatalyst between **3** and the bis(boronate) afforded macrocycle **4** in moderate yield with partial silyl deprotection observed. Next, TBAF deprotection of the remaining silyl ethers and subsequent aromatization using SnCl₂/HCl¹⁰ afforded **5** cyclo(3,9)-perylenehepta(paraphenylene), a fragment of a (10,8) CNT. The structure of **5** was confirmed

through ¹H and ¹³C NMR spectroscopy as well as mass spectrometry.

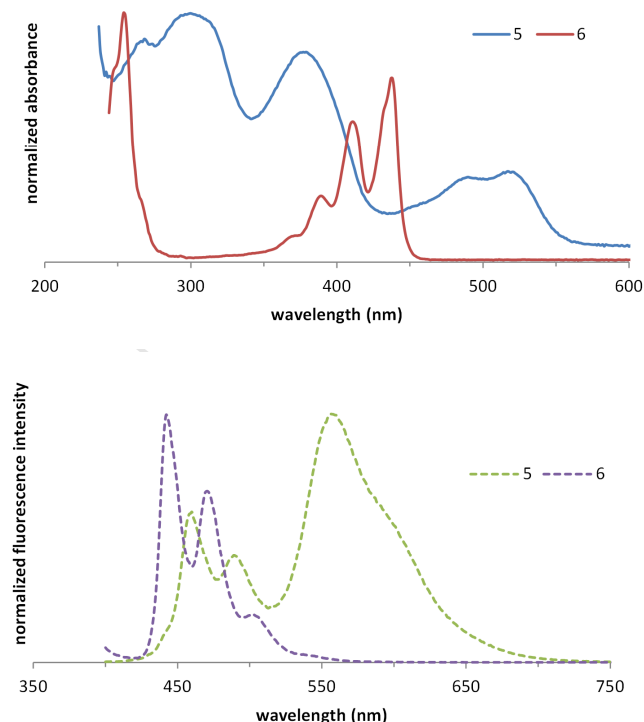
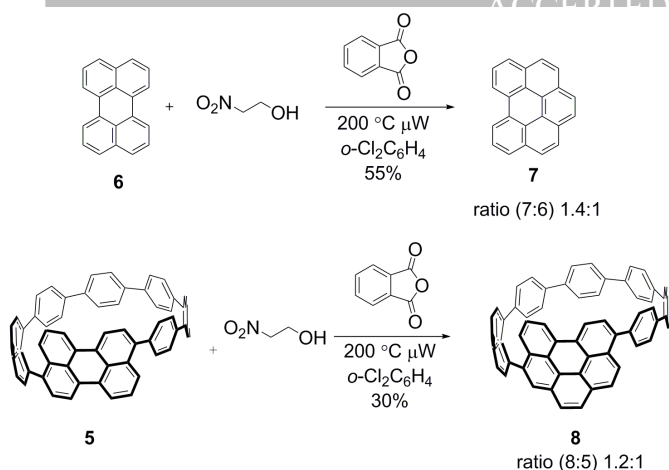


Figure 3: UV-Vis and fluorescence of perylene CPP and flat perylene in methylene chloride

Notably the UV-Vis spectrum of **5** compared to flat perylene (**6**) shows significantly red shifted absorbance. The λ_{max} value for the most intense absorption of **5** is 313 nm with an absorption coefficient of $4.05 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Unlike many CPPs, the HOMO-LUMO transition is not symmetry forbidden¹¹ and we observe an absorbance at 518 nm ($\epsilon = 1.23 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) which was corroborated with time-dependent DFT (TD-DFT) calculations. We also observe a red shifted fluorescence for **5** compared to flat perylene. The unique photophysical behavior of **5** warrants further investigation (Figure 3). The quantum yield for **5** was 0.21 which is significantly lower than previously reported value of 0.94 for flat perylene¹², however, is comparable to similarly sized [8]CPP (0.10) and [9]CPP (0.38).¹³ We also observed much greater solubility of **5** in common organic solvents compared to **6**.

With our desired target molecule in hand, we next examined the Diels-Alder reactivity of the system. Diethyl acetylenedicarboxylate was initially employed as a dienophile using similar conditions to what Scott had previously reported.^{4d} Although we found the diester to be reactive, the benzannulated



Scheme 2: Diels-Alder on perylene (**6**) and cyclo(3,9)-perylenehepta(paraphenylene) (**8**)

product rapidly decomposed on silica gel proving difficult to isolate and characterize. Additionally, we examined *in situ* generated nitroethylene^{4c} and found it also appeared to undergo cycloaddition and rearomatization with **5** (Scheme 2). Unfortunately, all efforts to separate the benzannulated product (**8**) from the starting material were unsuccessful; however, examination of the ¹H NMR spectrum strongly suggests successful product formation based the appearance of multiple downfield shifted peaks which would be expected in that region from desymmetrization of the molecule (Figure 4). This trend is also observed when comparing perylene to benzo[ghi]perylene. Additionally, the MALDI-TOF spectrum shows a peak at 807 consistent with a [M+H]⁺ ion expected for **8**. Based on our identification of **8**, we can conclude the ratio of **8** to **5** is 1.2:1 in the isolated mixture, similar to what is observed when flat perylene is reacted under analogous conditions (Scheme 2). Although we were unsuccessful at isolating the benzannulated product, this study demonstrates that a Diels-Alder reaction is feasible on a curved aromatic system and it shows similar reactivity to when a planar substrate is employed.

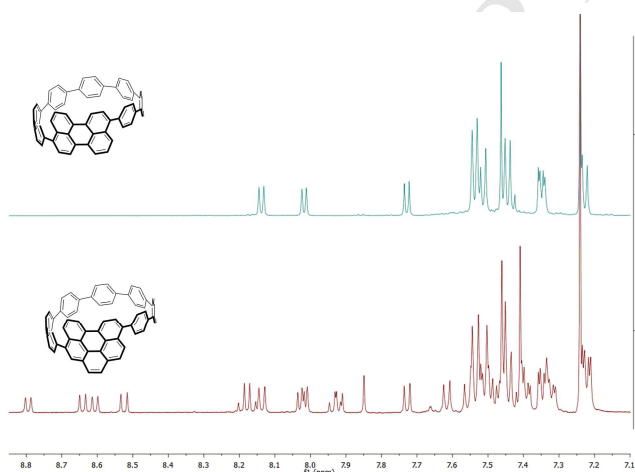


Figure 4: ¹H NMR of **5** and mixture of **8** and **5**

3. Summary and conclusions

In conclusion, we have synthesized a CPP incorporating a perylene moiety to investigate the reactivity of a Diels-Alder reaction as a viable means for CNT growth. Nitroethylene acts as

a masked acetylene equivalent and is a reactive dieneophile for cycloaddition on the bay region of perylene incorporated into a macrocyclic structure. These results show that perylene incorporated into a macrocycle displays similar reactivity to the flat substrate (at least for this macrocyclic ring size) suggesting that Diels-Alder cycloaddition is a viable strategy for nanotube growth when using an appropriate template.

4. Experimental

Unless otherwise noted all reactions were conducted in flame-dried or oven dried (120 °C) glassware with magnetic stirring under an atmosphere of dry nitrogen. All reagents were used as received. ¹H and ¹³C NMR spectra were obtained on a Varian INOVA-500, Bruker Avance III-HD 500, or Bruker Avance II-HD 600 spectrometer. Chemical shifts of ¹H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.24 ppm). Chemical shifts of ¹³C NMR spectra were recorded in ppm from the central peak of CDCl₃ (77.0 ppm) on the δ scale. Absorbance spectra were obtained using dichloromethane as the solvent in a 1 cm quartz cuvette on an Agilent Cary 60 UV-Vis spectrophotometer. Emission spectra were collected using dichloromethane as the solvent in a 1 cm quartz cuvette using a Horiba Jobin Yvon FluoroMax-4 spectrophotometer. THF, toluene and DMF were dried by filtration through alumina according to the methods described by Grubbs.¹⁵ 1,2-Dichlorobenzene (Aldrich anhydrous) was used as received. Silica gel column chromatography was conducted with Zeochem Zeoprep 60 Eco 40-63 μm silica gel. Thin layer chromatography (TLC) was performed using Sorbent Technologies Silica Gel XHT TLC plates. Developed plates were visualized using UV light at wavelengths of 254 and 365 nm.

2, 4'-bromo-1-((triethylsilyl)oxy)-[1,1'-biphenyl]-4(1H)-one:

4'-bromo-1-hydroxy-[1,1'-biphenyl]-4(1H)-one (6.00 g, 22.6 mmol, 1 equiv) was combined with imidazole (3.07 g, 45.1 mmol, 2 equiv) in a 250 mL flask and dissolved in 112 mL DMF at room temperature. Et₃SiCl (5.2 g, 34.5 mmol, 1.5 equiv) was added dropwise to the solution. Following addition of Et₃SiCl, the flask was immersed in an oil bath and heated to 40 °C and stirred overnight. The reaction was allowed to cool to rt then quenched with saturated aqueous NaHCO₃ and extracted with EtOAc. The aqueous phase was extracted 3x with EtOAc then the organic layer was washed with aqueous NaHCO₃, twice with H₂O, brine, and dried with Na₂SO₄. Solvent was removed *in vacuo* and the crude residue was purified via flash chromatography on silica gel (10% EtOAc/hexanes) to afford a faint yellow oil (8.00 g, 92%). ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 10.0 Hz, 2H), 6.20 (d, *J* = 10.0 Hz, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 6.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 185.6, 151.5, 139.1, 131.8, 127.2, 126.7, 122.1, 72.8, 6.9, 6.2. HRMS (CI⁺) (*m/z*): calculated for C₁₈H₂₃SiO₂Br 378.0651 found 378.0653. IR (film, cm⁻¹): 2953, 2874, 1670, 1628, 1484.

3, the corresponding dibromide¹⁰ (5.00 g, 7.68 mmol, 1 equiv) was dissolved in 200 mL THF and cooled to -78 °C over 1 hour. After cooling, nBuLi (2.5 M in hexanes, 15.2 mmol, 2 equiv) was added to the solution over 1 min and allowed to stir for 2 min after which ketone **2** (5.77 g, 15.2 mmol, 2 equiv) was quickly injected. The reaction was stirred at -78 °C for 1 hour then quenched with 10 mL H₂O and allowed to warm to rt. The reaction was diluted with EtOAc and the organic phase was washed with H₂O, brine, and then dried with Na₂SO₄. Solvent was removed *in vacuo* and the crude reaction mixture was purified via flash chromatography (5% EtOAc/hexanes) affording the major diastereomer as a white solid (4.81 g, 50%).

¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, *J* = 8.6 Hz, 4H), 7.34 (s, 8H), 7.23 – 7.19 (m, 4H), 6.01 (d, *J* = 10.0 Hz, 4H), 5.97 (s, 4H), 5.91 (d, *J* = 10.0 Hz, 4H), 2.04 (s, 2H), 0.97 (t, *J* = 7.9 Hz, 18H), 0.91 (t, *J* = 7.9 Hz, 18H), 0.67 (q, *J* = 7.9 Hz, 12H), 0.59 (q, *J* = 7.9 Hz, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 145.7, 144.8, 143.0, 132.7, 131.5, 131.2, 130.1, 127.4, 126.1, 125.4, 121.1, 71.3, 71.2, 69.1, 7.1, 7.0, 6.5, 6.4. MALDI-TOF (*m/z*) [*M*]⁺ calculated for C₆₆H₉₀Br₂O₆Si₄ 1248.4 found 1248.1, IR (film, cm⁻¹): 3373, 2951, 2874, 1675, 1483

4, Dibromide **3** (1.00 g, 0.799 mmol, 1 equiv), 3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene (402 mg, 0.797 mmol, 1 equiv), and SPhos Pd G2 (115 mg, 0.159 mmol, 0.2 equiv) were dissolved in 240 mL dioxane and heated to 80 °C. 25 mL (degassed) 2 M K₃PO₄ (aq) was added to the solution and allowed to stir over night. Dioxane was removed *in vacuo* and the crude reaction mixture was dissolved in CH₂Cl₂ and washed with H₂O, brine, dried over Na₂SO₄ and solvent removed *in vacuo*. The crude residue was purified by flash chromatography (30% EtOAc/hexanes) affording a yellow solid (147 mg, 17%). Note: partial deprotection of the silyl ether was observed. ¹H NMR (600 MHz, CDCl₃) δ 8.12 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.33–7.30 (m, 2H), 7.29 – 7.27 (m, 6H), 7.23 – 7.10 (m, 16H), 6.33 (dd, *J* = 10.2, 2.4 Hz, 2H), 6.21 (dd, *J* = 10.1, 2.4 Hz, 2H), 6.14 (dd, *J* = 10.1, 2.3 Hz, 2H), 5.91 (dd, *J* = 10.1, 2.4 Hz, 2H), 2.10 (s, 2H), 1.24 (s, 2H), 1.04 (t, *J* = 7.9 Hz, 18H), 0.73 (q, *J* = 7.7 Hz, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 143.4, 142.0, 140.3, 140.0, 139.9, 139.3, 135.6, 133.4, 132.6 (2), 131.1, 130.3, 129.8, 129.3, 128.6, 128.0, 127.5, 127.1, 126.6, 126.5, 126.2, 125.9, 120.2, 119.4, 72.4, 69.8, 29.7, 7.2, 6.5. MALDI-TOF (*m/z*) [*M*]⁺ calculated for C₇₄H₇₂O₆Si₂ 1112.5; found 1112.2 IR (film, cm⁻¹): 3340, 2923, 1589, 1506, 1358

5, Macrocyclic **4** (118 mg, 0.106 mmol, 1 equiv) was dissolved in 5 mL THF at room temperature and TBAF (1 M in THF, 0.424 mmol, 4 equiv) was added. The reaction was stirred for 2 h and then quenched with H₂O, diluted with THF, and washed with brine. The organic layer was dried over Na₂SO₄ and filtered through a pad of silica eluting with 20% MeOH/CH₂Cl₂ and solvent removed *in vacuo*. Next, aqueous HCl (48 μL, 0.58 mmol, 6.6 equiv) was added to a solution of SnCl₄·2H₂O (65 mg, 0.29 mmol, 3.3 equiv) in 8 mL THF. The solution was allowed to stir for 15 min at room temperature. The solution was then transferred via syringe to a flask containing the crude deprotected macrocycle from above and allowed to stir overnight in the dark. The reaction was quenched with 10% NaOH (aq) and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na₂SO₄, and solvent removed *in vacuo*. The crude residue was purified via flash chromatography (40% CH₂Cl₂/hexanes) affording a red solid (47 mg, 68%). ¹H NMR (600 MHz, CDCl₃) δ 8.14 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.48 (m, 12H), 7.48 – 7.38 (m, 10H), 7.36–7.33 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 140.1, 139.5, 138.7, 138.2, 138.0, 137.7, 137.5, 136.9, 131., 131.3, 130.4, 129.6, 129.1, 128.7, 128.5, 128.1, 127.5, 127.4, 127.1, 127.0, 126.4, 126.2, 121.6, 119.2. MALDI-TOF (*m/z*) [*M*]⁺ calculated for C₆₂H₃₈ 782.3; found 782.1 IR (film, cm⁻¹): 3024, 2923, 1591, 1485, 1387, 1262

8, **5** (9.0 mg, 0.011 mmol, 1 equiv) and phthalic anhydride (43 mg, 0.29 mmol, 25 equiv) were charged to a microwave vial. The vial was evacuated and refilled with N₂ 3 times. 2-nitroethan-1-ol (91 mg, 0.29 mmol, 25 equiv) was added and the mixture was dissolved in 350 μL 1,2-Dichlorobenzene. The vial was heated to 200 °C for 20 h and the mixture was diluted with CH₂Cl₂ and solvent was removed *in vacuo*. The crude residue was purified by

flash chromatography (35% CH₂Cl₂/pentane) affording a mixture of **8** and **10** with a combined mass of 5.0 mg (ratio **8**:**5**, 1.2:1) Characteristic peaks of **8** ¹H NMR (500 MHz, CDCl₃) δ 8.79 (d, *J* = 7.8 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 8.9 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H). MALDI-TOF (*m/z*) [*M*+H]⁺ calculated for C₆₄H₃₉ 807.3; found 807.1.

7, Benzo[*ghi*]perylene, perylene (25 mg, 0.099 mmol, 1 equiv) and phthalic anhydride (367 mg, 2.5 mmol, 25 equiv) were charged to a microwave vial. The vial was evacuated and refilled with N₂ 3 times. 2-nitroethan-1-ol (225 mg, 0.29 mmol, 25 equiv) was and the mixture was dissolved in 4 mL 1,2-Dichlorobenzene. The vial was heated to 200 °C for 20 h and the mixture was diluted with toluene and solvent was removed *in vacuo*. The crude residue was purified by flash chromatography (10% CH₂Cl₂/hexanes) affording a mixture of product and starting material (25 mg, ratio 1.39:1, 55% yield). Spectral data matched as previously reported.¹⁶

3,9-dibromoperylene : Following a modified literature procedure, perylene (5.90 g, 23.4 mmol, 1 equiv) was dissolved in 900 mL benzene in a 2 L flask equipped with a base trap at 80 °C. The mixture was allowed to cool to 35 °C (note-some perylene precipitated out of solution) and Br₂ (17.3 g, 109 mmol, 4.7 equiv) was added dropwise over 10 min and the reaction was stirred at 35 °C for 1 hour then cooled to room temperature. The precipitate was filtered and recrystallized 4x in 5/3 aniline/toluene then washed with acetone affording an orange solid (2.1 g, 26%) ¹H NMR (600 MHz, CDCl₃) δ 8.24–8.21 (m, 2H), 8.12 (dd, *J* = 8.4, 0.9 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.59 (dd, *J* = 8.4, 7.5 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 133.2, 131.1, 130.9, 130.8, 129.6, 127.9, 127.5, 123.1, 121.4, 121.1. HRMS (CI⁺) (*m/z*): calculated for C₂₀H₁₀Br₂ 407.9149; found 407.9156 IR (film, cm⁻¹): 3047, 1931, 1846, 1777, 1599 characteristic ¹H peaks of minor isomer ¹H NMR (600 MHz, CDCl₃) δ 8.26 (d, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H).

3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene 3,9-dibromoperylene (1.00 g, 2.44 mmol, 1 equiv), B₂Pin₂ (1.54 g, 6.06 mmol, 2.5 equiv), Pd(dppf)Cl₂ (175 mg, 0.239 mmol, 0.1 equiv), and finely ground KOAc (1.41 g, 14.4 mmol, 6 equiv) were combined in a dry flask. The flask was then evacuated and backfilled with N₂ 3 times. 25 mL of toluene was added to the mixture and the flask was heated to 80 °C and allowed to stir overnight. The mixture was cooled to room temperature then filtered through a pad a celite eluting with ethyl acetate. Solvent was removed *in vacuo* and the crude residue was purified via flash chromatography (5% EtOAc/Hexanes) affording a yellow solid (370 mg, 31%) ¹H NMR (600 MHz, CDCl₃) δ 8.67 (dd, *J* = 8.4, 1.0 Hz, 2H), 8.25 (m, 2H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.53 (dd, *J* = 8.4, 7.5 Hz, 2H), 1.42 (s, 24H). ¹³C NMR (151 MHz, CDCl₃) δ 138.3, 136.3, 134.4, 131.0, 129.1, 128.4, 126.8, 120.8, 119.5, 83.7, 25.0. HRMS (ES⁺) (*m/z*): [*M*+Na]⁺ calculated for C₃₂H₃₄B₂O₄Na 527.2552 found 527.2568 IR (film, cm⁻¹): 2974, 1588, 1506, 1370. ¹H peaks of minor isomer ¹H NMR (600 MHz, CDCl₃) δ 8.64 (d, *J* = 8.3 Hz, 2H), 8.22–8.20 (m, 4H)

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Supplementary Data

¹H & ¹³C spectra, computational details, and photophysical data are available in the Supplementary Data.

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