

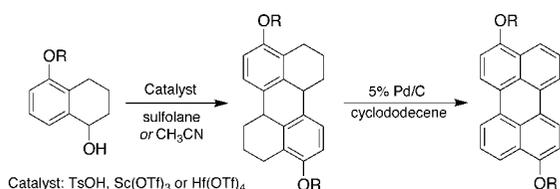
Tandem Friedel–Crafts Annulation to Novel Perylene Analogues¹

Mark A. Penick, Mathew P. D. Mahindaratne,
Robert D. Gutierrez, Terrill D. Smith, Edward R. T. Tiekink,
and George R. Negrete*

Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249

george.negrete@utsa.edu

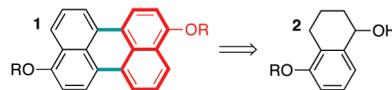
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Novel dialkyloxy- and dihydroxyoctahydroperylene are regioselectively available via a new tandem Friedel–Crafts alkylation of tetrahydronaphthalene precursors followed by oxidative aromatization. Heating of 5-alkyloxy-1-tetralol with *p*-toluenesulfonic acid in sulfolane gave the corresponding octahydroperylene in moderate yields. Studies with Lewis acids and tetralin-1,5-diol in acetonitrile at room temperature provided the 4,10-dihydroxy analogue cleanly, albeit in reduced yields. Examples of these new series of perylene analogues were partially oxidized to the corresponding contiguously aromatic, anthracene core products or fully aromatized to 3,9-dialkyloxyperylene in good yields.

Perylene and its derivatives² are important as organic solar cell photoacceptors,³ fluorescent labels for analytical applications,⁴ molecular sensors,⁵ and components for flat-panel displays,⁶ molecular electronics,⁷ and solid-state lighting.⁸ In some photovoltaic materials, perylene photoemission initiates an electron cascade that results in an electric current.⁹ Com-

SCHEME 1. Tandem Friedel–Crafts Annulation Approach



mercially available perylene diimides¹⁰ and their derivatives¹¹ are widely employed in these studies.¹² Alkyloxy-substituted perylenes¹³ are attractive targets since they are expected to stabilize perylene radical cation intermediates, resulting in improved photoacceptor properties. Here we describe a regioselective synthesis of 3,9-dialkyloxyperylene (**1**; Scheme 1) based on a new tandem Friedel–Crafts alkylation of tetrahydronaphthols.

Tandem reactions are important processes in organic chemistry because of their pragmatic value and aesthetic appeal.¹⁴ Those that involve a Friedel–Crafts reaction in prelude to a second transformation have been reported,¹⁵ however, domino

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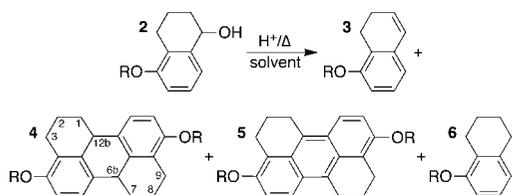
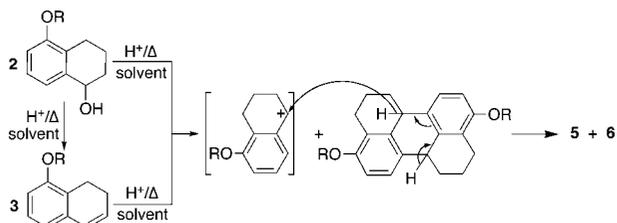
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SCHEME 2. Products from Tandem Friedel–Crafts Alkylation of Tetrahydronaphthols

SCHEME 3. Mechanism of Redox Conversions to 5 and 6


Friedel–Crafts reactions are unknown. Recognizing that the perylene skeleton consists of peri-annulated naphthalenes (Scheme 1), we considered a novel route to the perylene core via sequential Friedel–Crafts alkylations. The starting compounds, 5-methoxy- and 5-*n*-octyloxy-1,2,3,4-tetrahydro-1-naphthols (**2a**, R = CH₃, and **2b**, R = *n*-C₈H₁₇, respectively), are accessible from commercially available 5-methoxy-1-tetralone and 1,2,3,4-tetrahydronaphth-1,5-diol (**2c**, R = H), respectively. Domino Friedel–Crafts alkylations would result in an annulated, partially hydrogenated dialkyloxyperylene skeleton (**4**; Scheme 2) that can be oxidized to fully aromatic perylene **1**. Here we describe results on the implementation of such an approach.

Upon heating in acidic condition (10 mol % TsOH, C₆H₆, 70 °C, 6 h), **2a** (R = Me) generated corresponding olefin **3a** initially,¹⁶ but under more vigorous conditions (100 mol % TsOH, C₆H₅Cl, 132 °C, 22 h) a greenish-yellow crystalline precipitate was obtained, which was isolated by filtration (33% mass yield).¹⁷ The initial analysis of the solid by ¹H and ¹³C NMR was consistent with a mixture of octahydroperylene **4a** (90% of the mixture), a self-condensate of **2a**, and a small amount of fluorescent bluish green **5a** (<10%; Scheme 2). Mass spectrometry data supported the assignments of both structures. Product **4a** was eventually isolated and fully characterized (*vide infra*).

The isolation of 5-methoxy-1,2,3,4-tetrahydronaphthalene (**6a**, R = Me) from the filtrate suggested the involvement of **2a** or **3a** in the oxidation of **4a** to **5a**. It is likely that the benzylic cation derived under acidic conditions from **2a** or **3a** abstracts a hydride from **4a** to initiate its conversion to **5a** (Scheme 3). Thus, this oxidation occurs upon concomitant reduction of **2a** (or **3a**) to **6a**. In accord with this suggestion, oxidation of **4a** under hydride abstraction conditions (excess Ph₃CCl and lutidine, sulfolane, 120–165 °C, N₂) generated a mixture rich in **5a** (**4a** to **5a** ratio was shown to be 26:74), which began to precipitate upon cooling below 110 °C.

Several experiments were conducted to improve the modest tandem Friedel–Crafts annulation yields (Table 1). As men-

tioned above, use of **2a** with benzene resulted in formation of olefin **3a** only, with no evidence of product **4a** (entry 1). Reaction in refluxing chlorobenzene gave **4a** in modest yield and good selectivity (see entry 2; 9:1 ratio of **4a** to **5a**), though at higher temperature. Use of nitrobenzene as solvent at 150 °C gave no evidence of product. A similar result was obtained in sulfolane at 132 °C where the starting material and products were destroyed after 22 h of heating giving only a black solution containing traces of **4a** and **5a** (entry 3). In an identical reaction monitored by TLC **2a** gave **4a** and **5a** in 40% yield and in 1:2 ratio within 2 h (entry 4). Upon employment of the *n*-octyloxy analogue (**2b**), prepared via alkylation of the commercially available 1,5-diol (**2c**), the reaction gave a poor result, as determined by ¹H NMR spectroscopy (entry 5). At reduced temperature (95 °C), however, reaction of **2b** in sulfolane gave **4b** and **5b** (ratio of 83:17) in 55% total yield within 26 h (entry 6). In addition, it was observed that at a higher mole percent of catalyst used, the formation of **4b** and **5b** dominated over **3b** (entries 6–8). These reactions were also improved upon use of inert atmosphere, in that less **5b** was formed (cf. entry 6 versus entries 9 and 10).

A sample with a high percentage of **4b** (entry 10) was recrystallized in toluene and subjected to single-crystal X-ray diffraction analysis.¹⁸ The monomer exhibits antiannulation coupling at the dibenzylic positions (C-6b and C-12b; Scheme 2) and extended octyloxy chains.^{18a}

Oxidation of the mixture of **4a** and **5a** (entry 2; Table 1) to 3,9-dimethoxyperylene (**1a**, R = CH₃, Scheme 4) occurred upon treatment with 10% Pd/C/cyclododecene.¹⁹ The solid product was insoluble in CHCl₃ and DMSO but was sparingly soluble in THF. The oxidation product was identified by mass spectrometry (*m/z* 312) and ¹H and 2D COSY NMR spectra, but poor solubility precluded the collection of ¹³C NMR data. The poor solubility of this compound contrasts sharply with its precursors **4a** and **5a**, both of which were readily *dissolved* in CDCl₃, and is likely a consequence of strong stacking associations.

To afford increased perylene solubility, **4b** (R = *n*-C₈H₁₇) was prepared from **2b** with use of the TsOH/sulfolane system under N₂ (entries 9–12; Table 1). Although the reaction time was as much as 25 h, the optimized reaction condition (3.6 mmol; entry 10) allowed near exclusive formation of **4b** (97% of the isolated mixture) in satisfactory yield (63%; entry 10). When the reaction was further scaled up to 27 mmol the products were isolated in the same ratio (93:7) with slightly reduced yield (56%; entry 12) compared to 1 mmol scale (entry 9). As anticipated,^{17b} **3b** also formed the product mixture of **4b** and **5b** (70:30 ratio) in 40% yield under the same conditions. The mixture was subsequently aromatized¹⁹ to produce **1b** in 90% yield (R = *n*-C₈H₁₇; Scheme 4), which was *soluble* in a wide range of organic solvents as anticipated. Spectroscopic analysis including NMR, FT-IR, UV, and MS confirmed the formation of novel **4b** and its oxidized form 3,9-dioctyloxyperylene (**1b**).

Tandem Friedel–Crafts reactions of 1,5-diol **2c** with TsOH in sulfolane produced intractable mixtures. On the other hand, saturated solutions of **2c** in CH₃CN (0.3 M) and Lewis acids (0.015 equiv of Sc(OTf)₃ or Hf(OTf)₄, or 0.30 equiv of La(OTf)₃)²⁰ at ambient temperature gave modest yields of diol

(16) The acid catalyzed elimination of **2** to **3** occurs under mild conditions compared to the tandem Friedel–Crafts alkylations. Thus, it is possible that this reaction proceeds via the intermediacy of **3**.

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(18) (a) For all crystallographic data of **4b** see the Supporting Information, pp 13–24: (a) Crystal structure of **4b** (page 13). (b) Molecular packing of the unit cell of **4b** (page 13).

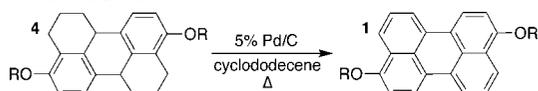
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TABLE 1. Preparation of Octahydroperylene Derivatives^a

entry	subst./mol% TsOH	solvent /temp (°C)/time (h)	product(s) ^{b,c}			isolated yield ^d
			3	4	5	
1	2a/10	C ₆ H ₆ /70/6	99	0	0	90
2	2a/100	C ₆ H ₅ Cl/132/22	0	9	<1	33
3	2a/100	sulfolane/132/12.5	0	tr	tr	0
4	2a/100	sulfolane/132/2.0 ^e	f	f	f	40 (34:66)
5	2b/100	sulfolane/132/12.5	tr	5	11	0
6	2b/100	sulfolane/95/25	9	35	10	55 (83:17)
7	2b/50	sulfolane/95/25	12	58	10	55 (83:17)
8	2b/20	sulfolane/95/26	4	1	tr	29 (80:20)
9	2b/100	sulfolane/95/22 ^g	6	53	10	59 (93:7)
10	2b/100	sulfolane/95/25 ^{g,h}	f	f	f	63 (97:3)
11	2b/50	sulfolane/95/25 ^{g,h}	6	33	1	58 (97:3)
12	2b/100	sulfolane/95/22 ^{g,i}	f	f	f	56 (93:7)
13	2c/1.5 ^j	CH ₃ CN/25/24 ^g	f	f	f	29 (<99:1)

^a All reactions were performed in 0.5 M (1 mmol scale) in air unless otherwise noted. ^b Starting material **2a** (R = CH₃; entries 1–4), **2b** (R = *n*-C₈H₁₇; entries 5–12), or **2c** (R = H; entry 13) not detected in TLC (5% EtOAc/hexanes) after indicated reaction time. ^c Ratio of crude mixture determined by ¹H NMR after workup. ^d Combined yield of the mixture of **4** and **5** (ratio in parentheses). ^e Reaction performed in 2.0 mmol scale. ^f NMR ratios not determined. ^g Reaction performed under N₂. ^h Reaction performed in 3.6 mmol scale. ⁱ Reaction performed on 27 mmol scale. ^j Reaction performed in 0.3 M solution with Hf(OTf)₄ as the catalyst.

SCHEME 4. Synthetic Route to Prepare 3,9-Dialkyloxyperylene



4c (19%, 29%, and 27% isolated yields, respectively) along with complex mixtures of unidentified byproducts. The precipitation of **4c** from these reaction mixtures allowed its facile isolation without chromatography. Solvent (ether, acetone, THF, EtOAc, CH₃NO₂) or temperature variation (0–70 °C), or changes in the addition protocol did not improve these results. It is noteworthy that the availability of phenolic **4c** (R = H) enables access to diverse perylene analogues.

In summary, domino Friedel–Crafts alkylation/self-condensation of tetrahydronaphthol analogues generated partially hydrogenated dialkyloxyperylene frameworks, which were readily oxidized to anthracenyl and perylenyl products. The self-condensation can be performed under relatively mild conditions with easily accessible substrates. Additional investigations on the photophysical and photochemical properties of these novel alkyloxyperylene are ongoing and will be reported in due course.

Experimental Section

5-Methoxy-1,2,3,4-tetrahydro-1-naphthol (2a).²¹ Prepared from 5-methoxy-1-tetralone as a white solid in 74% yield, mp 69–72 °C (lit.^{21a} mp 74–79). ¹H NMR (300 MHz):^{21b} δ 7.19 (t, 1H, *J* = 8 Hz), 7.06 (d, 1H, *J* = 8 Hz), 6.76 (d, 1H, *J* = 8 Hz), 4.82–4.72 (m, 1H), 3.82 (s, 3H), 2.82–2.69 (m, 1H), 2.61–2.47 (m, 1H), 2.01–1.71 (m, 4H), 1.69 (d, 1H, *J* = 6 Hz). ¹³C NMR:^{21b} δ 18.0 (t), 22.9 (t), 31.7 (t), 55.3 (q), 68.1 (d), 108.6 (d) 120.5 (d), 126.0 (s), 126.5 (d), 140.0 (s), 157.0 (s). IR (cm⁻¹): 3326, 2935, 1580, 1466, 1427, 1312, 1248, 1042, 1015, 788, 729.

5-(1-Octyloxy)-1,2,3,4-tetrahydro-1-naphthol (2b). To a flask containing 1,2,3,4-tetrahydronaphthal-1,5-diol (**2c**; 10.00 g, 61

mmol) in DMF (100 mL) under N₂ was added K₂CO₃ (8.93 g, 65 mmol) and 1-bromooctane (11 mL, 63 mmol). The mixture was heated to 55–60 °C for 4 days while being monitored by TLC (silica gel, 5% ethyl acetate/hexanes). More K₂CO₃ (1.62 g, 11.7 mmol) and 1-bromooctane (1.4 mL, 8 mmol) were added and heating was continued for another day. The product was extractively isolated and purified by crystallization (hexanes) to give 22.5 g of **2b** as a white solid (74% yield), mp 54–56 °C. ¹H NMR: δ 7.16 (t, 1H, *J* = 8.2 Hz), 7.04 (d, 1H, *J* = 8.2 Hz), 6.73 (d, 1H, *J* = 8.2 Hz), 4.80–4.73 (m, 1H), 3.98–3.91 (m, 2H), 2.84–2.72 (m, 1H), 2.62–2.48 (m, 1H), 2.03–1.69 (m, 6H), 1.63 (d, 1H, *J* = 3.9 Hz), 1.54–1.40 (m, 2H), 1.40–1.18 (m, 8H), 0.94–0.82 (m, 3H). ¹³C NMR: δ 14.1 (q), 18.0 (t), 22.6 (t), 23.0 (t), 26.2 (t), 29.2 (t), 29.3 (t), 31.7 (t), 31.8 (t), 67.8 (t), 69.1 (d), 109.4 (d) 120.2 (d), 126.1 (s), 126.2 (d), 140.0 (s), 156.4 (s). MS (*m/z*): 276 (M⁺, 22), 258 (M⁺ – H₂O, 45), 146 (M⁺ – H₂O – C₈H₁₆, 100), 145 (M⁺ – H₂O – C₈H₁₇, 63). IR (cm⁻¹): 3361, 2919, 2852, 1582, 1459, 1308, 1245, 1077, 1039, 1016, 783, 691. Exact mass analysis calcd for C₁₈H₂₉O₂ (MH⁺) 277.2168, found 277.2165.

General Preparation of Octahydroperylene 4. Aryl ether alcohol **2** (10.0 mmol) and *p*-toluenesulfonic acid monohydrate (1.95 g, 10.3 mmol) in sulfolane (20 mL) under N₂ were heated (at 132 °C for **2a** and at 95 °C for **2b**) for an appropriate time (2.0 h for **2a** and 22 h for **2b**) with stirring. The reaction mixture was allowed to cool to room temperature and the resultant precipitate was separated by filtration. The solid was further purified by crystallization (EtOAc/CH₂Cl₂) to obtain **4** (with a detectable amount of **5**) as a greenish yellow solid in both cases.

4,10-Dimethoxy-1,2,3,6b,7,8,9,12b-octahydroperylene (4a). Prepared from **2a** in 37% yield (90:10 ratio of **4a**:**5a**) as a greenish yellow solid, mp 249–252 °C dec. ¹H NMR: δ 7.26 (d, 2H, *J* = 8.3 Hz), 6.84 (d, 2H, *J* = 8.3 Hz), 3.85 (s, 6H), 3.76–3.70 (m, 2H), 3.10 (ddd, 2H, *J* = 5.1, 7.1, 16.1 Hz), 2.58–2.47 (m, 4H), 2.05 (ddq, 2H, *J* = 5.1, 13.2, 8.1 Hz), 1.74 (dddd, 2H, *J* = 3.9, 7.1, 13.4, 8.5 Hz), 1.51 (tt, 2H, *J* = 8.5, 12.4 Hz). ¹³C NMR: δ 20.8 (t), 21.0 (t), 29.8 (t), 36.0 (d), 55.6 (q), 108.6 (d), 124.6 (d), 126.2 (s), 127.9 (s), 136.8 (s), 154.4 (s). MS (*m/z*): 320 (M⁺, 95), 319 (M⁺ – H, 70), 289 (M⁺ – H – 2CH₃ and M⁺ – OCH₃, 100). IR (cm⁻¹): 2929, 2859, 2835, 1602, 1487, 1463, 1346, 1259, 1081, 1002, 800, 753. Calcd for C₂₂H₂₅O₂ (MH⁺) 321.1855, found 321.1853.

4,10-Bis(1-octyloxy)-1,2,3,6b,7,8,9,12b-octahydroperylene (4b). Prepared from **2b** in 60% yield (98:2 ratio of **4b**:**5b**) as a greenish yellow solid, mp 125–127 °C. ¹H NMR: δ 7.23 (d, *J* = 9.0 Hz),

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6.81 (d, $J = 9.0$ Hz), 4.01–3.92 (m, 4H), 3.75–3.69 (m, 2H), 3.16–3.08 (m, 2H), 2.58–2.46 (m, 4H), 2.09–1.99 (m, 2H), 1.84–1.69 (m, 6H), 1.56–1.43 (m, 6H), 1.40–1.24 (m, 16H), 0.92–0.86 (m, 6H). ^{13}C NMR: δ 14.1 (q), 20.9 (t), 21.1 (t), 22.7 (t), 26.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.8 (t), 31.8 (t), 36.0 (d), 68.3 (t), 109.7 (d), 124.5 (d), 126.5 (s), 127.8 (s), 136.8 (s), 153.9 (s). MS (m/z): 516 (M^+ , 50), 387 ($\text{M}^+ - \text{C}_8\text{H}_{17}\text{O}$, 100), 275 ($\text{M}^+ - \text{C}_8\text{H}_{17}\text{O} - \text{C}_8\text{H}_{16}$, 50). IR (cm^{-1}): 2940, 2917, 2848, 1604, 1581, 1465, 1395, 1344, 1261, 1081, 999, 795, 754. Calcd for $\text{C}_{36}\text{H}_{53}\text{O}_2$ (MH^+) 517.4046, found 517.4042. Single-crystal X-ray analysis at 223(2) K: triclinic crystal system (space group $P\bar{1}$) with unit cell dimensions $a = 4.608(2)$ Å, $b = 9.424(4)$ Å, $c = 17.933(7)$ Å, $\alpha = 90.869(5)^\circ$, $\beta = 95.234(10)^\circ$, $\gamma = 103.709(9)^\circ$, $V = 752.8(6)$ Å³, $Z = 1$, and $D_x = 1.140$ g/cm³.

4,10-Dihydroxy-1,2,3,6b,7,8,9,12b-octahydroperylene (4c). A mixture of 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (2c; 166 mg, 1.01 mmol) and hafnium(IV) trifluoromethanesulfonate (12 mg, 0.015 mmol) in acetonitrile (3 mL) was stirred at room temperature for 30 h. Precipitated solid was separated by centrifugation, washed once with fresh acetonitrile (2 mL), and again with acetonitrile/methanol (1:1; 2 mL) to obtain **4c** in 29% yield as a white solid, mp >300 °C dec. ^1H NMR ($\text{DMSO}-d_6$): δ 8.98 (s, 2H), 7.06 (d, 2H, $J = 8.3$ Hz), 6.72 (d, 2H, $J = 8.8$ Hz), 3.60–3.54 (m, 2H), 2.94 (ddd, 2H, $J = 4.9, 6.8, 15.6$ Hz), 2.47 (ddt, 2H, $J = 12.2, 8.3, 4.4$ Hz), 2.38 (dt, 2H, $J = 15.6, 8.3$ Hz), 1.97 (dtt, 2H, $J = 4.9, 8.3, 10.2$ Hz), 1.63–1.53 (m, 2H), 1.26 (tt, 2H, $J = 8.3, 12.2$ Hz). ^{13}C NMR ($\text{DMSO}-d_6$): δ 20.5 (t), 20.7 (t), 29.7 (t), 35.3 (d), 113.0 (d), 123.4 (s), 124.4 (d), 125.7 (s), 136.3 (s), 151.7 (s). MS (m/z): 292 (M^+ , 11), 275 ($\text{M}^+ - \text{H}_2\text{O}$, 4), 263 ($\text{M}^+ - \text{CH}_3\text{O}$, 8), 91 (C_7H_7^+ , 100). IR (cm^{-1}): 3261, 2946, 2863, 1591, 1456, 1373, 1299, 1243, 948, 803, 606. Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2$ (MH^+) 293.1536, found 293.1545.

4,10-Dimethoxy-1,2,3,7,8,9-hexahydroperylene (5a). A mixture of **4a** and **5a** (40 mg; ~5:1 ratio) was heated with 2,6-lutidine (9 equiv), chlorotriphenylmethane (8 equiv), and *p*-toluenesulfonic acid (0.66 equiv) in sulfolane at 120–165 °C for 5 h. Upon cooling, a **5a**-rich mixture (~74% of **5a**) crystallized. The crystals were separated by filtration in 77% yield as a golden solid, mp >260 °C dec. ^1H NMR: δ 8.09 (d, $J = 9.3$ Hz), 7.35 (d, $J = 9.6$ Hz), 3.98 (s, 6H), 3.50 (t, $J = 6.3$ Hz), 3.13 (t, $J = 6.3$ Hz), 2.16 (quintet, $J = 6.3$ Hz). ^{13}C NMR: δ 22.4 (t), 23.6 (t), 26.9 (t), 56.9 (q), 114.7 (d), 120.7 (s), 122.7 (d), 125.5 (s), 127.2 (s), 128.6 (s), 150.5 (s). MS (m/z): 318 (M^+ , 100), 303 ($\text{M}^+ - \text{Me}$, 55). IR (cm^{-1}): 3066,

3008, 2962, 2839, 1581, 1501, 1385, 1248, 1138, 1109, 1038, 823, 762, 684. Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_2$ (MH^+) 319.1698, found 319.1695.

3,9-Dimethoxyperylene (1a). A mixture of **4a** and **5a** (350 mg, 1.1 mmol), 10% Pd/C (38 mg), and cyclododecene (0.65 mL, 3.5 mmol) in mesitylene (10 mL) was heated at 150–155 °C overnight under N_2 . Product **1a** was isolated as a golden solid after workup (257 mg, 75%), mp >300 °C. ^1H NMR ($\text{THF}-d_8$): δ 4.02 (s, 6H), 6.94 (d, 2H, $J = 8.3$ Hz), 7.40 (dd, 2H, $J = 7.6, 8.3$ Hz), 7.97 (dd, 2H, $J = 1.0, 8.3$ Hz), 8.16 (dd, 2H, $J = 1.0, 7.4$ Hz), 8.17 (d, 2H, $J = 8.3$ Hz). IR (cm^{-1}): 1583, 1503, 1386, 1250, 1040, 825, 805, 764. MS (m/z): 312 (M^+ , 100), 297 ($\text{M}^+ - \text{Me}$, 96), 282 ($\text{M}^+ - 2\text{Me}$, 40). Calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2$ (M^+) 312.1150, found 312.1147.

3,9-Bis(1-octyloxy)perylene (1b). A mixture of **4b** and **5b** (461 mg, 0.89 mmol), 5% Pd/C (53 mg), and cyclododecene (0.86 mL, 4.46 mmol) in mesitylene (13.5 mL) was refluxed under N_2 for 5 h. Product **1b** was isolated as a bright yellow solid after workup (410 mg, 90%), mp 219–220 °C. ^1H NMR: δ 0.95–0.85 (m, 6H), 1.46–1.21 (m, 16H), 1.64–1.50 (m, 4H), 6.84 (d, 2H, $J = 8.6$ Hz), 7.44 (t, 2H, $J = 7.7$ Hz), 8.12–8.01 (m, 6H). Due to its low solubility at room temperature, it was necessary to acquire the ^{13}C NMR spectrum of **1b** at 47 °C. Additional peaks beyond the 18 expected were seen, which suggest the formation of isomeric π -stacked dimers. ^{13}C NMR: δ 14.0, 22.7, 26.3, 29.27, 29.38, 29.43, 31.9, 68.4, 77.1, 105.84, 105.87, 119.5 (br), 120.3 (br), 120.6 (br), 124.1, 125.9 (br), 126.0 (br), 126.8, 129.4, 131.6, 154.8. UV (hexanes, nm): 457, 428, 404. IR (cm^{-1}): 3062, 2924, 2582, 1582, 1503, 1467, 1380, 1252. MS (APCI): m/z 508 (M^+). Elemental Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{O}_2$: C, 84.99; H, 8.72. Found: C, 85.12; H, 8.81.

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Supporting Information Available: Proton and ^{13}C NMR spectra of new compounds and crystallographic data for **4b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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