Supplementary material for:

A new functionalization strategy for pentacene

John E. Anthony,* Johannes Gierschner, Chad A. Landis, Sean R. Parkin, Jes B. Sherman and Ronald C. Bakus II

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini (200 Mhz) spectrometers. Proton chemical shifts were referenced to $CDCl_3$ (7.26 ppm). ^{13}C resonances were referenced to $CDCl_3$ (77.0 ppm). Chemicals were purchased from Aldrich Chemical Company (Milwaukee, WI) or Acros Organics (Pittsburgh, PA). All moisture sensitive reactions were carried out in flame-dried glassware cooled under dry nitrogen. Cyclohexanol was dried by azeotropic distillation from benzene. TLC was carried out on Merck Silica Gel 60 plates. Melting Points were recorded (uncorrected) on a Thomas-Hoover Capillary Melting Point Apparatus. Absorbance spectra were obtained with a Shimadzu UV-2501PC UV-Vis recording spectrophotometer. Electrochemical measurements were performed using a BAS CV-50W potentiostat. Silica gel Chromatography was performed on Sorbent Technologies silica gel (230 - 450 mesh).

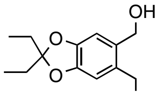
Synthesis of dioxolanes 4: 11.3 g (50 mmol) of dimethyl 4,5-dihydroxyphthalate[1] was dissolved in 50 mL of benzene. To this solution was added 55 mmol of the desired ketone and 1 g of *p*-toluenesulfonic acid. The solution was heated to reflux overnight in a Dean-Stark apparatus. After the collection of water ceased, the reaction solution was diluted with 200 mL of CH_2Cl_2 and washed with water (2 x 100 mL). The organic layers were dried over $MgSO_4$ and the solvent was removed by rotary evaporation. GC/MS analysis showed the product to be a mixture of diester and anhydride, carried on to the next step without separation.

Synthesis of dioxolane-dimethanols 6. The mixture of dioxolane dimethylphthalate and dioxolane phthalic anhydride (~ 40 mmol) was dissolved in anhydrous THF (20 mL) and to this solution was added dropwise 48 mL of a 1.0 M solution of $LiAlH_4$ in THF. The mixture was stirred for 4 hr., then heated at reflux for an additional 4 hours. The solution

---

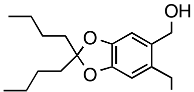
[1] Anderson, D. R.; Koch, T. H. *J. Org. Chem.* **1978**, *43*, 2726.

was then cooled to 0 °C, and quenched by the dropwise addition of water (2 mL), 10 % NaOH (2 mL), and another addition of water (6 mL). The aluminum salts were removed by filtration and washed with THF (50 mL). The solvent was removed by rotary evaporation, and the product purified by chromatography on silica gel.



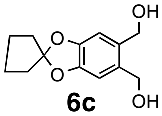
6a

Diethyl dimethanol **6a** was isolated as a pale yellow oil (98%). ^{1}H NMR ($CDCl_3$) δ 6.71 (s, 2 H), 4.57 (s, 4 H), 2.73 (s, 2 H), 1.88 (q, 4 H, J = 7.6 Hz), 0.94 (t, 6 H, J = 7.8 Hz). MS (m/z, EI) 238 [M^+, 20%], 209 [M^+ -Et, 100%]. Anal. Calc. for $C_{13}H_{18}O_4$: C, 65.52; H, 7.61. Found C, 65.56; H, 7.31.



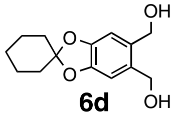
6b

Dibutyl dimethanol **6b** was isolated as a pale yellow oil (69%). ^{1}H-NMR ($CDCl_3$) δ 6.72 (s, 2H), 4.53 (s, 4H), 3.66 (broad s, 2H), 1.86 (m, 4H), 1.39 (m, 4H), 1.31 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 12H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 148.1, 132.7, 121.8, 109.8, 63.88, 37.67, 24.87, 22.83, 14.06. MS (m/z, EI): 294 [M^+, 9%], 276 [M^+ - H_2O, 14%], 237 [M^+ - Bu, 83%]



6c

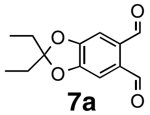
Cyclopentylidine dimethanol **6c** was purified by chromatography on silica gel (5:1 hexanes/CH_2Cl_2, then CH_2Cl_2, then ether) and isolated as a pale yellow oil (63%). ^{1}H-NMR ($CDCl_3$) δ 6.76 (s, 2H), 4.61 (s, 4H), 2.88 (m, 2H), 2.08 (m, 4H), 1.84 (m, 4H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 147.5, 133.0, 128.2, 110.1, 64.16, 37.24, 23.42.
MS (m/z, EI): 236 [M^+, 21%], 218 [M^+ - H_2O, 40%], 207 [M^+ - HCO, 37%]



6d

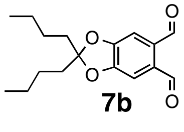
Cyclohexylidine dimethanol **6d** was recrystallized from 1,2-dichloroethane to yield pale yellow needles (m.p. 88 °C) (88%). ^{1}H NMR ($CDCl_3$) δ 6.68 (s, 2 H), 4.49 (s, 4 H), 3.82 (ws, 2 H), 1.84 (t, 4 H, J = 4 Hz), 1.67 (m, 4 H), 1.44 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 147.0, 132.5, 119.0, 110.0, 63.43, 35.00, 24.39, 23.01. MS (m/z, EI): 250 [M^+, 28%], 216 [M^+ - H_2O, 45%], 205 [M^+ - HCO, 35%]. Anal. Calc. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24. Found C, 67.25; H, 6.97.

Synthesis of dioxolane dialdehydes 7.[2] To an oven-dried 250-mL flask cooled under nitrogen was added oxalyl chloride (4.3 mL, 34 mmol) dissolved in CH_2Cl_2. The mixture was cooled to -78 °C and a solution of DMSO (4.8 mL, 68 mmol) in CH_2Cl_2 (4.5 mL) was added dropwise. After stirring for 10 min., a second solution containing the dimethanol (16 mmol) dissolved in CH_2Cl_2/DMSO (4 mL) was added dropwise. After 30 min. of stirring, 38 mL (264 mmol) Et_3N was added and the temperature was maintained for 10 min. more. The solution allowed to warm to room temperature overnight, then was poured into ice-cold water (80 mL) and extracted with CH_2Cl_2 (2 x 200 mL). The organic layers were dried over $MgSO_4$ and the solvent was removed by rotary evaporation.



7a

Diethyl dialdehyde **7a:** Silica chromatography (1:1 hexanes : CH_2Cl_2) yielded 71% of **7a** as a dark yellow oil. ^{1}H NMR ($CDCl_3$) δ 10.5 (s, 2 H), 7.30 (s, 2 H), 1.97 (q, 4 H, J = 8 Hz), 0.97 (t, 6 H, J = 7.8 Hz). MS (m/z, EI) 234 [M^+], 205 [M^+ -Et, 45%], 177 [M^+ - EtCO, 100%]. Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found C, 66.44; H, 6.06.

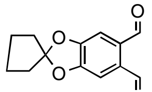


7b

---

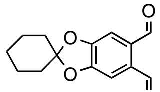
[2] Farooq, O. *Synthesis* **1994**, 1035.

Dibutyl dialdehyde **7b** was purified on silica gel that had been deactivated by rinsing with 5% triethylamine / dichloromethane solution, eluting first with 5:1 hexanes:CH_2Cl_2 then 1:1 hexanes:CH_2Cl_2 to provide **7b** as a yellow oil in 91% yield. ^{1}H-NMR ($CDCl_3$) δ 10.50 (s, 2H), 7.33 (s, 2H), 1.97 (m, 4H), 1.38 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 12H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 190.1, 152.9, 133.1, 124.9, 108.9, 37.86, 24.67, 22.74, 14.06. MS (m/z, EI): 290 [M^+, 26%], 262 [M^+ - CO, 5%], 233 [M^+ - Bu, 79%]



7c

Cyclopentylidine dialdehyde **7c**. The resulting oil was purified by chromatorgraphy using deactivated silica gel (elution with hexanes and 9:1 hexanes:CH_2Cl_2) yielding 89% of a yellow solid (m.p. 88 – 91 °C). ^{1}H-NMR ($CDCl_3$) δ 10.49 (s, 2H), 7.27 (s, 2H), 2.17 (m, 4H), 1.89 (m, 4H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ 190.1, 152.2, 133.2, 131.2, 109.3, 37.49, 23.41. MS (m/z, EI): 232 [M^+, 26%], 203 [M^+ - HCO, 14%], 175 [M^+ - Bu, 37%]



7d

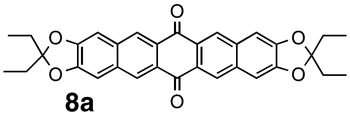
Cyclohexylidine dialdehyde **7d.** Column chromatography (silica gel, 1:1 hexanes : CH_2Cl_2) yielded 60 % of **7d** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 10.44 (s, 2 H), 7.29 (s, 2 H), 1.92 (m, 4 H), 1.75 (m, 4 H), 1.51 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 189.8, 152.0, 132.9, 122.4, 109.4, 35.18, 24.15, 22.90. MS (m/z, EI): 246 [M^+, 20%], 217 [M^+ - HCO, 19%]. Anal. Calc. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found C, 68.55; H, 6.10.

Synthesis of pentacene-6,13-quinones 8.[3] 10 mmol of the appropriate dialdehyde was dissolved in ethanol (20 mL) at 60 °C with stirring. 5.5 mmol of 1,4-cyclohexanedione was added and stirred with heating until it dissolved and then the solution was cooled to room temperature. 15 % KOH (1 mL) was added and the product immediately began to precipitate. The mixture was stirred vigorously at room temperature overnight. The

---

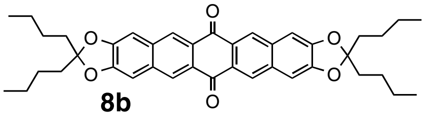
[3] W. Ried, F. Anthofer, *Angew. Chem.* 1953, **65**, 601.

quinone was collected by filtration, washed with methanol then ether, and dried in an oven at 65 °C.



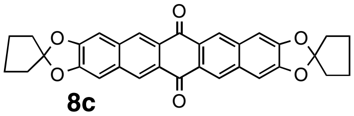
8a

Bis(diethyl dioxolane) pentacenequinone **8a:** 52% yield (m.p. 138 °C (dec)), MS (m/z, EI): 508 [M$^+$], 479 [M$^+$ -Et, 100%]. Anal. Calc. for $C_{32}H_{28}O_6$: C, 75.57; H, 5.54. Found C, 75.46; H, 5.00.



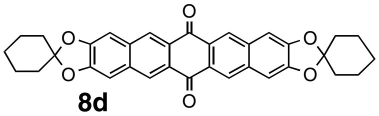
8b

Bis(dibutyl dioxolane) pentacenequinone **8b**: 62% yield (m.p. 266 – 267 °C), MS (m/z, EI): 620 [M$^+$, 8%], 563 [M$^+$ - Bu, 100%]. Anal. Calc. for $C_{40}H_{44}O_6$: C, 77.39; H, 7.14. Found C, 77.54; H, 7.05.



8c

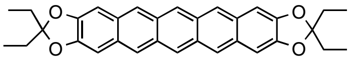
Bis(cyclopentylidine dioxolane) pentacenequinone **8c.** 39% yield, m.p. > 300 °C (dec.). MS (m/z, EI): 504 [M$^+$, 54%], 476 [M$^+$ - CO, 355], 475 [M$^+$ - HCO, 100%]. Anal. Calc. for $C_{32}H_{24}O_6$: C, 76.18; H, 4.79. Found C, 75.70; H, 5.01.



8d

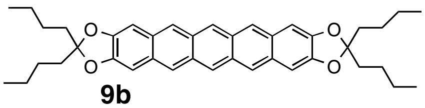
Bis(cyclohexylidine dioxolane) pentacenequinone **8d.** 58 % yield (m.p. 240 °C (dec)), MS (m/z, EI) 532 (M$^+$), 489 (M$^+$ -$CH_3CH_2CH_2$, 100%). Anal. Calc. for $C_{34}H_{28}O_6$: C, 76.67; H, 5.29. Found C, 75.40; H, 5.93.

Synthesis of dioxolane pentacenes 9:[4] In dry cyclohexanol (60 mL) was suspended 1.6 g (58 mmol) of aluminum foil, 0.065 g (0.24 mmol) of $HgCl_2$, and a small crystal of CBr_4. The suspension was heated at 140 °C for 12 h under N_2. To the solution was then added 2.4 mmol of pentacenequinone, and the resulting suspension heated at 140 °C for 6 – 24 hours (until all of the quinone had reacted). The reaction mixture was then cooled to room temperature, and poured into 300 mL of a rapidly stirred, 1:1 mixture of 10% (aq.) HCl / ethanol, and this suspension stirred vigorously for 30 min. The bright red pentacene was separated by filtration, washed with methanol and dried.



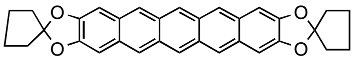
9a

Diethyl pentacene **9a** The red solid was further purified by elution through a short pad of silica gel (CH_2Cl_2) (yield = 23%). Melting point: 160 °C (dec). ^1H NMR ($CDCl_3$) δ 8.50 (s, 2 H), 8.16 (s, 2 H), 7.11 (s, 4 H), 1.77 (q, 8 H. 7.4 Hz), 0.93 (t, 12 H, 7.4 Hz). M.S. (m/z, MALDI, TCNQ matrix): 478. Anal. Calc. for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32. Found C, 80.05; H, 6.10.



9b

Dibutyl pentacene **9b** was further purified by chromatography on silica gel (CH_2Cl_2) to yield a bright red solid (67%) with melting point 140 °C (dec.). ^1H-NMR (400 MHz, CDCl3) δ 8.66 (s, 2H), 8.34 (s, 4H), 7.02 (s, 4H), 1.97 (t, J = 8.0 Hz, 8H), 1.48 (m, 8H), 1.39 (m, 8H), 0.91 (t, J = 7.2 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.3, 130.0, 129.5, 124.3, 123.9, 121.4, 100.7, 38.15, 24.96, 22.92, 14.18. MS (m/z, EI): 590 [M^+, 41%]. Anal. Calc. for $C_{40}H_{46}O_4$: C, 81.32; H, 7.85. Found C, 80.67; H, 6.52.

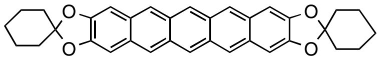


9c

---

[4] J. G. Laquindanum, H. E. Katz, A. J. Lovinger, *J. Am. Chem. Soc.* **1998**, *120*, 664.

Cyclopentylidine pentacene **9c** was triturated with hot DMF and dried to provide the insoluble pentacene derivative in 47% yield, m.p. 260 °C (dec.). MS (m/z, MALDI): 474 [M^+, 100%]



9d

Cyclohexylidine pentacene **9d** was crystallized from chlorobenzene as fine red needles (32%), m.p. 190 °C (dec). MS (m/z, MALDI): 502.2 [M^+]. Structure solved by X-ray crystallographic analysis.

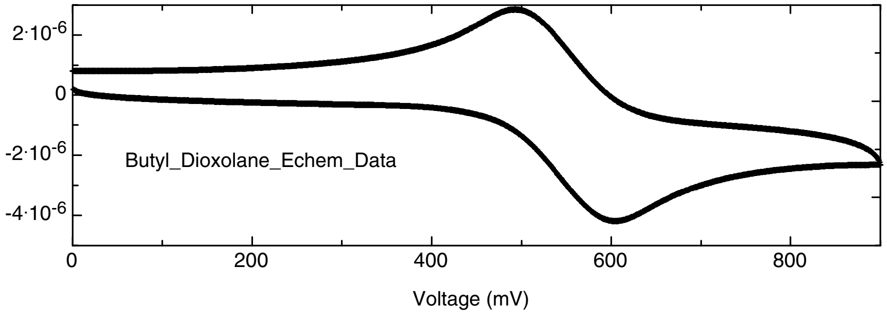
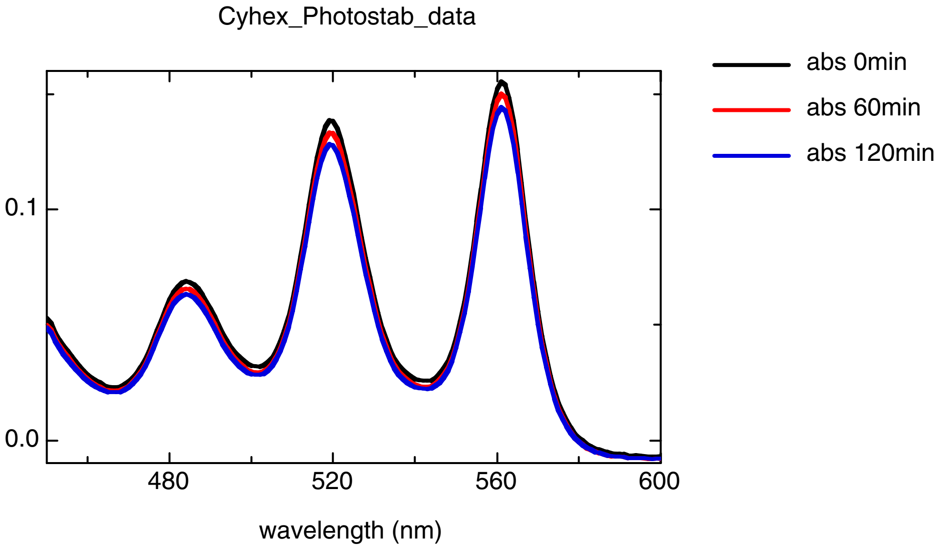


Figure S1. Representative cyclic voltammogram for pentacene **9b**. Scan rate: 100 mV / s.



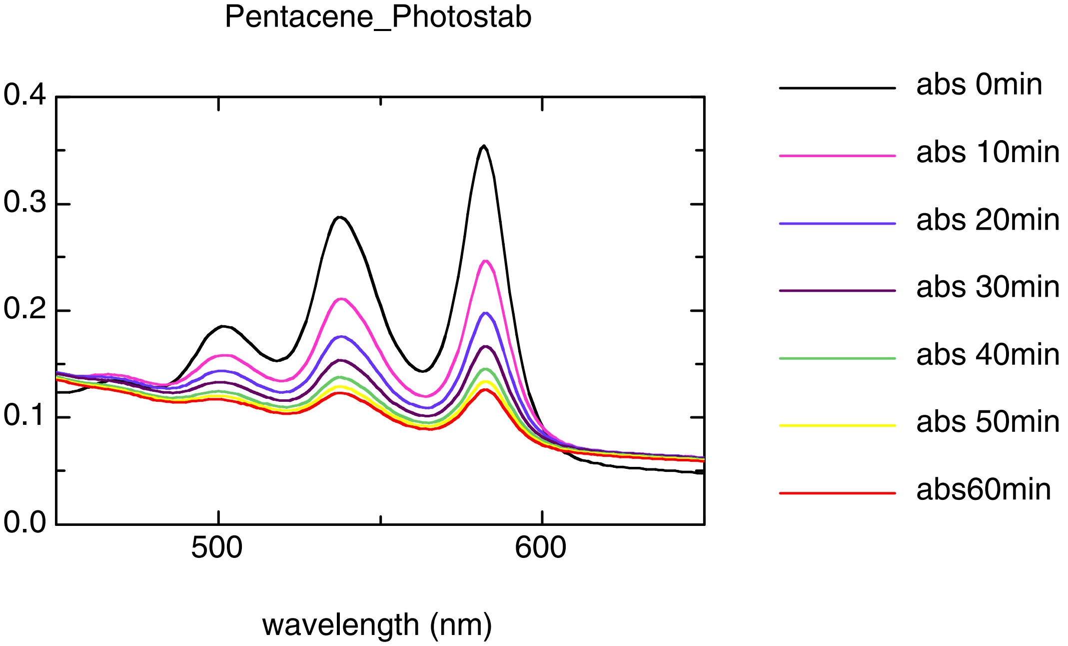


Figure S2. Comparison of the photostability of solutions of functionalized pentacene **9d** (top) and pentacene **1** (bottom).