Supporting material for:

Dehydrobenzoannulene/Dimethyldihydropyrene Hybrids: Model Systems for the Synthesis of Molecular Aromatic Probes

David B. Kimball, Michael M. Haley,* Reginald H. Mitchell, and Timothy R. Ward

Department of Chemistry, University of Oregon, Eugene, OR 97403-1253 and
Department of Chemistry, University of Victoria, PO Box 3065, Victoria, BC, Canada, V8W 3V6

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Varian Inova (^{1}H: 299.94 MHz, ^{13}C: 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual chloroform as internal standard (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm). Coupling constants are expressed in hertz. IR spectra were recorded using a Nicolet Magna FTIR 550 spectrometer. MS spectra were recorded using a Kratos MS50 spectrometer. UV-vis spectra were recorded on an HP 8453 UV-vis spectrophotometer. Et_3N was distilled from CaH_2 under an N_2 atmosphere prior to use. THF and Et_2O were distilled from Na and benzophenone under an N_2 atmosphere prior to use. All other chemicals were of reagent quality and used as obtained from manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230-400 mesh). Pre-coated silica gel plates were used for analytical (Baker, 200 X 50 X 0.25 mm) and preparative (Analtech, 200 X 200 X 1 mm) thin layer chromatography. Eluting solvents were reagent quality and used as obtained from the manufacturers**.** Reactions were carried out in an inert atmosphere (dry N_2 or Ar) when necessary. All deprotected terminal alkynes were used directly without further purification.

Bis[14]polyyne-DDP 5. ^{1}H NMR ($CDCl_3$) δ 9.07 (s, 4H), 7.73-7.70 (m, 4H), 7.59-7.56 (m, 4H), 7.33-7.25 (m, 8H), 1.66 (s, 18H), 0.94 (s, 84H), –3.39 (s, 6H); MS (FAB) *m/z* (%): 1466 (42) [M^+]. Limited solubility of **5** precluded ^{13}C NMR spectroscopy.

Bis[14]DBA-DDP 1. ^{1}H NMR ($CDCl_3$) δ 9.65 (s, 4H), 8.36 (d, *J* = 6 Hz, 4H), 7.70-7.65 (m, 8H), 7.55-7.50 (m, 4H), 1.95 (s, 18H), –3.33 (s, 6H); IR (KBr) 3059, 2962, 2924, 2865, 2220, 2161, 1474, 752 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 277 (43,700), 300 (45,700), 320 (42,700), 440 (46,800), 470 (74,100), 540 (15,800), 616 (2,600), 679 (2,700), 758 (10,700) nm; MS (MALDI) *m/z* (%): 837.90 (52) [M^+]. Limited solubility of **1** precluded ^{13}C NMR spectroscopy.

Tetrayne DDP 6. ^{1}H NMR ($CDCl_3$) δ 9.02 (s, 4H), 1.91 (septet, *J* = 6.9 Hz, 4 H), 1.67 (s, 18H), 1.15 (s, 24H), 1.04 (d, *J* = 6.9 Hz, 24H), 0.45 (s, 12H), 0.43 (s, 12H), –3.53 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 149.70, 139.07, 122.22, 117.99, 104.49, 103.43, 36.49, 34.59, 31.75, 30.62, 23.63, 21.06, 18.86, 15.72, –1.81; IR (KBr) 2959, 2925, 2864, 2136, 1249, 821, 772 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 265 (26,900), 288 (13,800), 295 (13,200), 307 (15,100), 314 (13,500), 327 (14,500), 405 (13,500), 432 (16,600), 504 (1,600), 728 (700) nm; HRMS (FAB) found, 1009.7274. Calcd for $C_{66}H_{105}Si_4$, 1009.7293.

Bis[18]polyyne-DDP 7. ^{1}H NMR ($CDCl_3$) δ 9.02 (s, 4H), 7.64-7.61 (m, 4H), 7.55-7.52 (m, 4H), 7.35-7.28 (m, 8H), 1.73 (s, 18H), 1.14 (s, 84H), –3.39 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 151.47, 140.52, 133.07, 132.43, 128.57, 127.92, 127.04, 125.15, 122.64, 117.65, 104.67, 96.18, 84.08, 83.45, 81.09, 78.55, 36.59, 31.73, 18.71, 11.29; IR (KBr) 3060, 2943, 2942, 2864, 2202, 2156, 1462, 756 cm^{-1}.

Bis[18]DBA-DDP 2. ^{1}H NMR ($CDCl_3$) δ 9.18 (s, 4H), 7.84-7.81 (m, 4H), 7.71-7.68 (m, 4H), 7.49-7.41 (m, 8H), 1.84 (s, 18H), –3.49 (s, 6H); IR (KBr) 3058, 2958, 2926, 2904, 2867, 2189, 2133, 752; UV-vis (CH_2Cl_2) λ_{max} (ε) 293 (70,800), 305 (74,100), 326 (74,100), 455 (107,000), 476 (166,000), 544 (46,800), 624 (6,600), 693 (6,600), 767 (39,800) nm; MS (FAB) *m/z* (%): 932 (15) [M$^+$]. Limited solubility of **2** precluded ^{13}C NMR spectroscopy.