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Supplementary ^{13}C, ^{31}P NMR data. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a 300 MHz spectrometer unless otherwise noted, and chemical shifts are given in δ (ppm) using solvent as internal reference, and the coupling constants are in Hertz (Hz).

Major α-epimers as bis-*p*-toluoyl esters of 1a-6a.

The major product **1a bis-toluoyl ester** was obtained as a pale yellow oil (α-epimer, 48% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.3, 21.4, 39.2, 64.5, 76.2, 78.0, 82.5, 122.3, 122.9, 123.2, 123.6, 126.0, 126.3, 126.4, 126.6, 126.8, 127.0, 128.7, 128.8, 128.9, 129.0, 129.2, 129.4, 129.6, 129.8, 130.6, 131.4, 136.2, 143.5, 143.6, 165.8, 166.2.

2a bis-toluoyl ester (α-epimer, 43% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.3, 21.4, 39.2, 64.5, 76.2, 78.0, 82.5, 122.3, 122.9, 123.2, 123.6, 126.0, 126.3, 126.4, 126.6, 126.8, 127.0, 128.7, 128.8, 128.9, 129.0, 129.2, 129.4, 129.6, 129.8, 130.6, 131.4, 136.2, 143.5, 143.6, 165.8, 166.2.

3a bis-toluoyl ester (α-epimer, 52% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.4, 21.5, 39.5, 64.5, 76.2, 77.8, 82.2, 122.1, 122.9, 125.1, 125.3, 125.8, 126.6, 127.0, 128.7, 128.8, 128.9, 129.2, 129.4, 129.5, 129.9, 133.6, 137.9, 143.6, 165.8, 166.2.

4a bis-toluoyl ester (α-epimer, 31% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.3, 21.4, 40.0, 64.4, 76.3, 80.2, 82.1, 122.1, 122.9, 125.1, 125.3, 125.8, 126.6, 127.0, 128.7, 128.8, 128.9, 129.2, 129.4, 129.5, 129.9, 133.6, 139.9, 143.8, 165.8, 166.3.

5a bis-toluoyl ester (α-epimer, 13% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 18.3, 19.0, 19.1, 21.4, 39.1, 64.4, 76.3, 77.2, 81.6, 125.9, 126.7, 126.8, 128.8, 128.9, 129.5, 131.1, 131.5, 133.7, 135.0, 137.3, 143.5, 143.6, 165.9, 166.1.

6a bis-toluoyl ester (α-epimer, 16% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 14.0, 20, 21.6, 39.4, 64.5, 74.8, 76.3, 82.5, 103.1 (t) 120.1 (dd), 125.2 (dd), 126.5, 126.8, 128.8, 128.9, 129.3, 129.5, 143.6, 143.8, 158.6, 158.7.

Epimerization of 1',2'-dideoxy-1'-α-aryl-3',5'-di-O-toluoyl-D-ribofuranoses and isolation of β-epimers.

6 bis-toluoyl ester (β-epimer, 46% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 13.8, 22.0 (d), 40.1, 64.9, 74.9, 83.0, 103.0 (t), 120.1 (d), 124.5 (d), 127.3 (d), 128.6, 128.8 (d), 128.9 (d), 144.0 (d), 156.5 (d), 158.0 (d), 155.9 (d), 162.3 (d), 166.1 (d).

1 bis-toluoyl ester (β-epimer, 38% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.4, 21.5, 41.3, 64.5, 77.1, 77.9, 82.7, 122.0, 122.4, 124.5, 124.8, 125.0, 125.6, 126.8, 126.9, 127.0, 127.2, 127.3, 127.5, 128.9, 129.0, 129.5, 129.6, 130.3, 130.6, 131.1, 133.9, 143.5, 143.9, 166.0, 166.2

2 bis-toluoyl ester (β-epimer, 28% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.4, 21.5, 40.4, 64.3, 76.9, 77.7, 82.4, 122.1, 122.8, 123.1, 123.4, 126.1, 126.4, 126.5, 126.8, 126.9, 128.7, 128.9, 129.0, 129.4, 129.5, 129.6, 129.8, 130.4, 131.3, 134.7, 143.5, 143.9, 166.0, 166.2.

3 bis-toluoyl ester (β-epimer, 37% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.4, 21.5, 40.6, 64.5, 77.0, 77.7, 82.4, 122.1, 122.8, 125.3, 125.4, 125.7, 125.9, 126.8, 126.9, 127.9, 128.6, 128.9, 129.0, 129.5, 130.2, 133.4, 136.3, 143.5, 143.9, 166.0, 166.2.

4 bis-toluoyl ester (β-epimer, 41% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 21.3, 21.4, 41.6, 64.5, 77.1, 80.7, 82.9, 123.5, 124.5, 125.6, 125.9, 126.8, 126.9, 127.4, 127.7, 128.1, 128.9, 129.3, 129.4, 129.5, 132.9, 133.0, 137.9, 143.5, 143.8, 165.9, 166.2.

5 bis-toluoyl ester (β-epimer, 54% isolated yield): ^{13}C NMR ($CDCl_3$, ppm) δ 18.2, 19.5, 22.1 (d), 41.0, 65.0, 82.5, 126.2, 127.0 (d), 128.6 (d), 128.8 (d), 132.1 (d), 135.5, 136.2, 1414.0, 144.5, 165.5, 166.0.

Deprotection of 1',2'-dideoxy-1'-aryl-3',5'-di-O-toluoyl-β-D-ribofuranoses.

nucleoside 2 (β-epimer, 74%): ^{13}C NMR ($CDCl_3$, ppm) δ 43.5, 63.8, 74.0, 78.0, 88.5, 123.4, 123.5, 124.0, 124.8, 127.1, 127.3, 127.4, 127.5, 129.6, 130.8, 131.0, 131.6, 132.8, 137.1.

nucleoside 3 (β-epimer, 50%): ^{13}C NMR ($CDCl_3$, ppm) δ 43.0, 63.0, 74.0, 77.0, 123.2, 124.0, 125.2, 125.4, 127.0, 127.5, 130.2, 134.8, 138.0.

nucleoside 4 (β-epimer, 68%): ^{13}C NMR ($CDCl_3$, ppm) δ 44.6, 63.9, 74.3, 81.5, 89.1, 125.1, 125.6, 126.6, 128.4, 128.6, 128.9, 134.3, 134.5, 140.4.

nucleoside 5 (β-epimer, 93%): ^{13}C NMR ($CDCl_3$, ppm) δ 19.0, 19.5, 19.6, 41.6, 63.0, 74.0, 77.0, 87.0, 126.2, 126.3, 131.2, 131.6, 134.1, 135.2, 137.0.

nucleoside 6 (β-epimer, 89%): ^{13}C NMR ($CDCl_3$, ppm) δ 12.2, 41.9, 62.2, 72.5, 73.2, 87.2, 101.59, 101.9, 102.3, 119.8, 119.9, 120.1, 124.1, 124.3, 128.8, 128.9, 129.0.

Preparation of 5'-O-tritylated β-C-nucleosides.

1 DMT ether was obtained as a yellowish foam in 64% yield (200 mg, 0.32 mmol): ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 43.9, 55.2, 64.5, 74.5, 77.5, 86.4 (d), 113.2, 122.8, 123.0, 124.8 (d), 125.0, 125.2, 125.9, 126.9, 127.2, 127.5, 127.6, 127.7, 128.0, 128.4, 130.2, 130.3, 130.6 (d), 131.5, 135.5, 136.1, 145.0, 158.5.

2 DMT ether (280 mg, 59%): ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 42.6, 55.1, 64.2, 74.1, 77.1 (obscured by solvent), 85.6, 86.0, 113.1, 122.3, 122.8, 123.2, 124.0, 126.2, 126.4, 126.5 (d), 126.8, 127.8, 128.2, 128.8, 129.7, 129.9, 130.1, 131.5, 136.0 (d), 136.2, 144.9, 155.8.

3 DMT ether (50 mg, 52%): ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 42.9, 55.1, 64.3, 74.3, 77.1 (obscured by solvent), 85.8, 86.2, 113.1, 122.2, 123.4, 125.4, 125.5, 125.9, 126.8, 127.7, 127.8, 128.2, 128.7, 130.1, 130.4, 133.6, 136.0, 137.7, 144.9, 158.4.

4 DMT ether (200 mg, 66%): n/d

5 DMT ether (311 mg, 92%): ^{13}C NMR ($CDCl_3$, ppm) δ 19.6, 19.8, 19.9, 43.1, 55.0, 64.0, 75.0, 82.2, 116.2, 125.3, 125.4, 125.6, 125.7, 130.0, 132.1, 132.2, 134.2, 135.2, 136.5, 145.0, 158.2.

6 DMT ether (350 mg, 88%): ^{13}C NMR ($CDCl_3$, ppm) δ 29.4, 42.5, 54.9, 64.3, 73.3, 74.3, 85.65, 102.3, 102.7, 103.0, 112.8, 115.0, 126.5, 127.5, 1127.6, 127.9, 128.1, 128.8, 128.9, 135.0, 145.0, 158.9.

Preparation of 3'-O-phosphoramidites.

DMT phosphoramidite 1 (210 mg, 81 %). ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 20.3 (m), 24.6 (m), 43.2 (m), 55.2, 58.3 (d), 64.1 (d), 75.8 (d), 76.0 (d), 77.9, 85.6(d), 86.3, 113.2, 117.7 (d), 122.8 (d), 123.1 (d), 124.8 (d), 125.1, 125.2, 125.9, 126.8, 127.1, 127.5, 127.6 (d), 127.8 (d), 127.9, 128.4, 130.3, 130.7 (d), 131.4, 135.4, 136.1 (d), 145.1, 158.5.

2 DMT phosphoramidite (280 mg, 77%): ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 20.0 (m), 24.5 (m), 42.0, 43.2 (m), 55.1, 58.4 (m), 63.9 (d), 75.3 (d), 75.8 (d), 77.2 (obscured by solvent), 85.0 (m), 86.2, 113.1, 117.5, 122.4, 123.0 (d), 123.2 (d), 124.1 (d), 126.2, 126.4 (d), 126.6 (d), 126.7 (d), 127.8, 128.3 (d), 128.8 (d), 129.7 (d), 129.9, 130.1 (d), 130.6, 131.6, 136.1 (m), 144.9, 158.4.

3 DMT phosphoramidite (48 mg, 50%): ^{13}C NMR 400MHz ($CDCl_3$, ppm) δ 20.3 (m), 24.5 (m), 42.0, 43.1 (m), 55.1, 58.4 (m), 63.9 (d), 75.1 (d), 76.2 (d), 77.1 (obscured by solvent), 85.0 (m), 86.1, 113.0, 122.3 (d), 123.4 (d), 125.4, 125.6 (d), 126.0 (d), 126.8 (d), 127.7, 128.2 (d), 128.6 (d), 130.1 (d), 130.5 (d), 133.6 (d), 136.0 (d), 137.5, 144.9, 158.4.

4 DMT phosphoramidite (170 mg, 65%): n/d

5 DMT phosphoramidite (380 mg, 89%): ^{31}P NMR ($CDCl_3$, ppm) δ 148.9, 148.4.

6 DMT phosphoramidite (420 mg, 84%): ^{31}P NMR ($CDCl_3$, ppm) δ 148.9, 148.3.

Crystallographic data. Crystals of nucleoside **3a** were obtained from CH_2Cl_2 / hexane. Measurements were made on an Enraf-Nonius diffractometer with graphite monochromated Mo-Kα radiation. Single crystals of $C_{15}H_{16}O_3$ are monoclinic, space group $P2_1$ (#4), with a = 7.806(2) Å, b = 6.720(2) Å, and c = 11.898(3) Å, V = 615.8(3) Å^3, Z = 2 with calculated density 1.31 g/cm^3. The data were collected at -20(1) °C using the $\omega/2\theta$ scan technique to a maximum 2θ of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 2.8°. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. A total of 1234 unique absorption-corrected reflections were collected, and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. The final cycle of full-matrix least-square refinement was based on 785 observed reflections and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement parameters of R = 0.043 and R_w = 0.039. The standard deviation of an observation of unit weight was 1.54. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.14 and -0.15 e-/Å^3, respectively. All calculations were performed with the teXsan software package of the Molecular Structure Corporation.

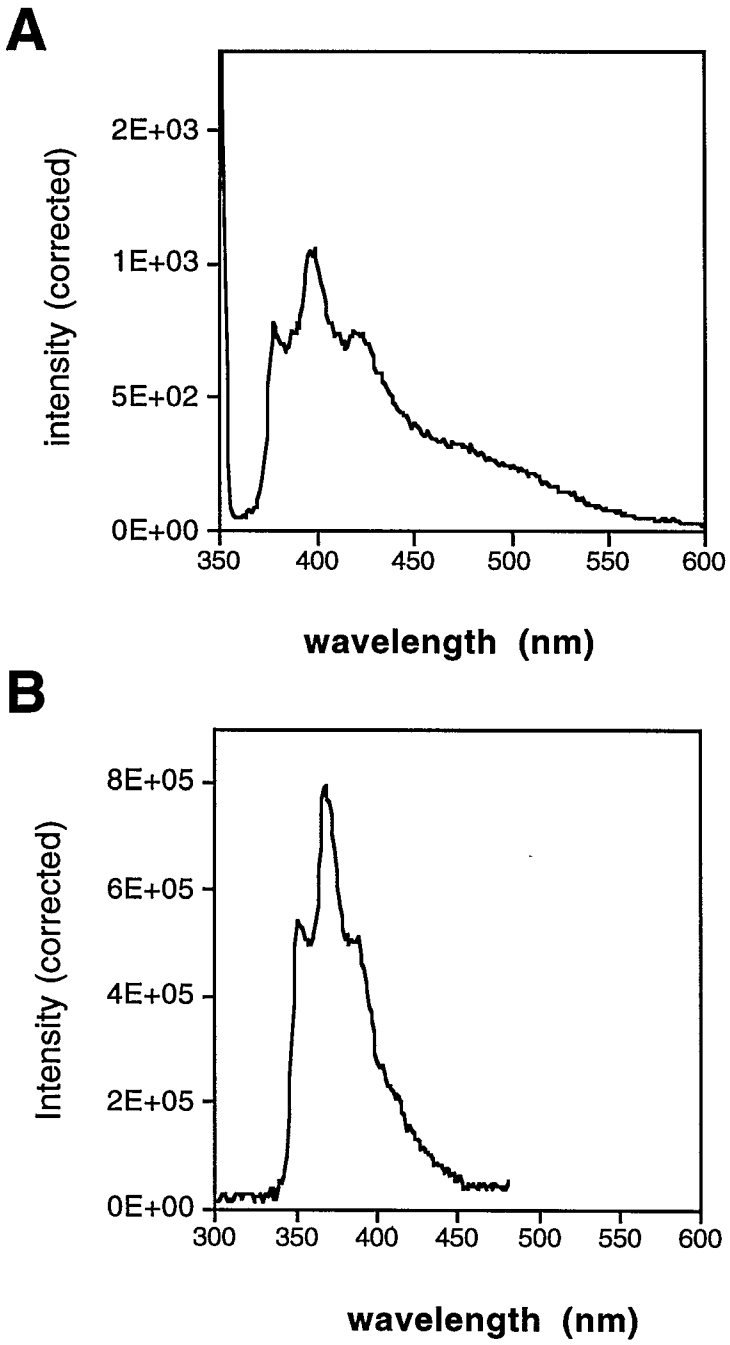

Figure 1 (supplemental). Fluorescence emission spectra for self-complementary heptamer oligonucleotides containing (**A**) pyrene (**1**) and (**B**) phenanthrene (**2**) as the C-nucleosides at the 5'-terminal position. The DNA sequence for both cases is 5'-XCGCGCG, where X is **1** or **2**. Excitation is at 341 and 251 nm, respectively, and solutions contain pH 7.0 PIPES (10 mM), 100mM NaCl, 10mM $MgCl_2$ and DNA strand concentrations of 0.1 and 0.15 μM. Experimental details are presented in the main text.