Supporting Information

Experimental Section

Deuterated chloroform ($CDCl_3$, D-99.8%) used for ^1H and ^{13}C NMR measurements was purchased from Cambridge Isotopes. ^1H and ^{13}C NMR spectra were acquired on either a Varian VT 500 MHz or a GE QE 300 MHz spectrometer.

The oligonucleotides used in the studies were custom synthesized by Integrated DNA Technologies, Inc. (IDT). PBS buffer 1x (pH 7.4, 11.9 mM phosphates, 137 mM NaCl, 2.7 mM KCl) was diluted from a 10x concentrated solution purchased from Fisher Scientific.

The effects of DNA oligonucleotides on the electronic spectra of compound **1** in aqueous solutions were obtained with a dual-beam Perkin Elmer Lambda 950 and software UV-WIN Lab version 5.1.5. Cuvette of 1-cm path length was used. Fluorescence spectra were acquired using a Jobin-Yvon Horiba Fluorolog 3-222 spectrophotometer and software FluorEssence.

***N*-(2-(*N'*,*N'*-diethylamino)ethyl)-9-piperazinyl-perylene-3,4-dicarboximide (1)**:

Piperazine (6.40 g, 74.4 mmol), 3.1 mL of DMSO, and 4.7 mL of xylene were added into a 50-mL round-bottom flask. The mixture was stirred at 80 °C for 1 h. 9-Bromo-*N*-(2-(*N',N'*-diethylamino)ethyl)perylene-3,4-dicarboximide **3** (0.50 g, 1.0 mmol) was added into the flask. The mixture was heated at 140 °C-160 °C for 3 days under N_2. Then the mixture was cooled to room temperature. CO_2-free double distilled water was added to the mixture. The precipitate formed was collected by suction filtration and washed with 5% KOH(aq) and double distilled water to remove excess solvent and piperazine. The solid residue was dried under vacuum overnight. The dried solid was then dissolved in $CHCl_3$ and purified by column chromatography over silica. The column was eluted with a mixture of chloroform and triethylamine (volume ratio = 8.5:1.5), and then a mixture of chloroform and ethylenediamine (volume ratio = 8.5:1.5). A purple solution was collected and the solvent was removed by evaporation under vacuum. The solid residue was suspended into a dilute KOH (3%) solution. The suspension was stirred at room temperature for 4 hours. Then a purple solid was collected by suction filtration and dried under vacuum overnight to afford **4.2** (0.39 g, 0.78 mmol, 78%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, 1H, ^3J (H, H) = 8 Hz, Ar-H), 8.27 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 8.18 (d, 1H, ^3J (H, H) = 8 Hz, Ar-H), 8.15 (d, 1H, ^3J (H, H) = 9 Hz, Ar-H), 8.12 (d, 1H, ^3J (H, H) = 8 Hz, Ar-H), 8.04 (d, 1H, ^3J (H, H) = 8 Hz, Ar-H), 7.97 (d, 1H, ^3J (H, H) = 8.5 Hz, Ar-H), 7.51 (t, 1H, ^3J (H, H) = 7.5 Hz, Ar-H), 7.09 (d, 1H, ^3J (H, H) = 8.5 Hz, Ar-H), 4.24 (t, 2H, ^3J (H, H) = 9 Hz, -CH_2), 3.20 (broad, 8H, Ar-NCH_2CH_2NH), 2.79 (t, 2H, ^3J (H, H) = 8 Hz, β-CH_2), 2.70 (q, 4H, 8 Hz, -NCH_2CH_3), 1.14 (t, 6H, ^3J (H, H) = 7.5 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, CH_3COOD): δ= 164.9, 164.8, 146.4, 152.4, 138.4, 132.3, 129.9, 129.5, 129.1, 129.0, 127.5, 127.5, 126.2,126.1, 125.5, 125.0, 120.8, 120.2, 120.0, 119.0, 117.4, 50.7, 49.5, 48.4, 45.2, 35.5, 9.0 ppm; UV-vis ($1.1x\ 10^{-5}$ M, CH_2Cl_2) λ_{max} = 538 nm (32800); IR (KBr): ν = 3086 (s), 2948 (m), 2818 (w), 1694 (m), 1649 (m), 1594 (s), 1568 (m), 1499 (m), 1451 (m), 1405 (s), 1358 (m), 1290 (s), 1245 (s), 1232 (s), 1160 (s), 1097 (s), 837 (s), 806 (s) cm^{-1}; mp 288 °C. The protonated forms **1a** and **1b** were prepared reaction of **1** with hydrochloric acid.