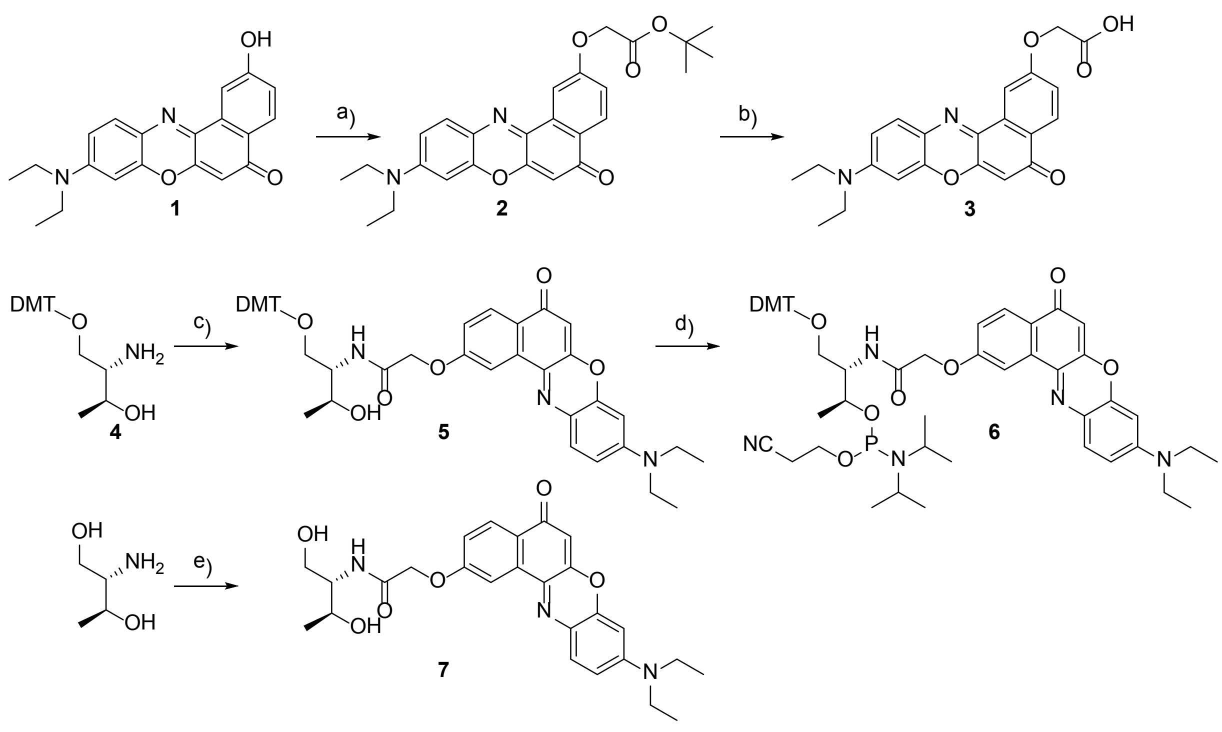
Supplementary Information

Preparation of supramolecular chromophoric assemblies using a DNA duplex.

Hiromu Kashida*, and Hiroyuki Asanuma



Scheme S1. Synthesis of phosphoramidite tethering biphenyl-4-carboxylic acid. Reagents and conditions: a) $ClCH_2CO_2{}^tBu$, K_2CO_3, acetone, reflux, 6h, 74%; b) TFA, Et_3SiH, CH_2Cl_2, rt, overnight, 86 %.; c) **3**, PyBOP, DIPEA, CH_2Cl_2, rt, overnight, 58 %.; d) $(iPr)_2NP(Cl)(OCH_2CH_2CN)$, Et_3N, THF, 0 °C → r.t., 1h, 91 %. e) **3**, DCC, HOBt, rt, overnight, 23 %.

The phosphoramidite monomer tethering Nile Red was synthesized as follows:

Compound **1** was synthesized according to the previous report.[1]

Compound **1** (0.73 g, 2.18 mmol), *tert*-butyl chloroacetate (0.63 ml, 4.38 mmol) and potassium carbonate (1.21 g, 8.75 mmol) were dissolved in 10 ml of acetone. After 6 hr of reflux, the solvent was removed in vacuo. Then the solid was redissolved in $CHCl_3$ and washed twice with brine. After drying over $MgSO_4$, the solvent was removed by evaporation, followed by silica gel column chromatography ($CHCl_3$: MeOH = 20:1, $R_f = 0.48$) to afford **3** (0.73 g, yield 74 %). ^{1}H-NMR [$CDCl_3$, 500 MHz] δ = 8.17 (d, $J = 9$ Hz, 1H), 7.94 (d, $J = 2.5$ Hz, 1H), 7.47 (d, $J = 9$ Hz, 1H), 7.17 (dd, $J = 2.5$Hz, 9 Hz, 1H), 6.56 (dd, $J = 3$ Hz, 9 Hz, 1H), 6.34 (d, 2.5 Hz, 1H), 6.22 (s, 1H), 4.69 (s, 2H), 3.38 (q, $J = 7.5$ Hz, 4H), 1.52 (s, 9H), 1.21 (t, J = 7 Hz, 6H). ^{13}C-NMR [$CDCl_3$, 126 MHz] δ = 183.2, 167.8, 160.6, 152.2, 151.0, 147.0, 139.6, 134.2, 131.2, 131.2, 128.0, 127.9, 126.4, 124.9, 118.7, 109.9, 109.7, 106.8, 106.6, 106.0, 105.4, 105.3, 104.8, 96.5, 96.3, 82.9, 66.0, 45.3, 28.3, 12.8. HRMS(FAB) Calcd for $C_{26}H_{29}N_2O_5$ (M+H$^+$) 449.2076. Found 449.2066.

Trifluoroacetic acid (3.2 ml, 42.4 mmol) was added to a solution of compound **2** (0.73 g, 1.63 mmol) and triethylsilane (1.3 ml, 8.17 mmol) in CH_2Cl_2 (10 ml). After vigorous stirring for overnight, the solvent was removed by evaporation, followed by silica gel column chromatography ($CHCl_3$: MeOH : AcOH = 100:10:1, $R_f = 0.08$) to afford **3** (0.55 g, yield 86 %). ^{1}H-NMR [$CDCl_3$, 500 MHz] δ = 8.00 (d, $J = 9$ Hz, 1H), 7.86 (d, $J = 2.5$ Hz, 1H), 7.55 (d, $J = 9$ Hz, 1H), 7.22 (dd, $J = 3$Hz, 9 Hz, 1H), 6.76 (dd, $J = 2.5$ Hz, 9.5 Hz, 1H), 6.61 (d, 3 Hz, 1H), 6.15 (s, 1H), 4.77 (s, 2H), 3.38 (q, $J = 7$ Hz, 4H), 1.16 (t, J = 7 Hz, 6H). HRMS(FAB) Calcd for $C_{33}H_{41}NO_5$ (M+H$^+$) 393.1450. Found 393.1434.

Compound **4** was synthesized according to the previous report.[2]

Compound **3** (0.55 g, 1.40 mmol) was reacted with PyBOP (0.89 g, 1.71 mmol) in CH_2Cl_2 (5.0 ml) for 10 min. Then, a solution of diisopropylethylamine (5.0 ml) and compound **4** (0.70 g, 1.72 mmol) in CH_2Cl_2 (5.0 ml) were added to the above mixture. After a night of vigorous stirring, the organic solution was washed with saturated aqueous solution of $NaHCO_3$. The solvent was removed by evaporation, followed by silica gel column chromatography (AcOEt : Et_3N = 100 : 3, $R_f = 0.33$) to afford **5** (0.64 g, yield 58 %). ^{1}H-NMR [$CDCl_3$, 500 MHz] δ = 8.14 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 2.5 Hz, 1H), 7.47 (d, J = 9 Hz, 1H), 7.40 (d, J = 7 Hz, 2H), 7.32 (d, J = 9 Hz, 1H), 7.26 (m, 6H), 7.18 (t, J = 7.5 Hz, 1 H), 7.11 (dd, J = 8.5 Hz, 2.5 Hz, 1H), 6.80 (m, 4H), 6.57 (dd, J = 9.5 Hz, 3 Hz, 1H), 6.36 (d, J = 2.5 Hz, 1H), 6.21 (s, 1H), 4.72 (d, J = 9.5 Hz, 1H), 4.67 (d, J = 10 Hz, 1H), 4.09 (m, 1H), 3.73 and 3.72 (s, 6H), 3.44-3.33 (m, 6H), 1.23 (t, J = 7 Hz, 6H) , 1.18 (d, J = 8.5 Hz, 3H). HRMS(FAB) Calcd for $C_{47}H_{47}N_3O_8$ (M^+) 781.3363. Found 781.3337.

DIPEA (0.29 ml, 1.66 mmol) and 2-cyanoethyldiisopropylchlorophosphoramidite (0.15 ml, 0.66 mmol) were added to a solution of compound **5** (0.26 g, 0.33 mmol) in THF (5.0 ml) at 0 ^{o}C. After 20 min of vigorous stirring on ice, the solution was stirred for 40 min at room temperature. Then, an excess of AcOEt was added to the reaction mixture and was washed with saturated aqueous solution of $NaHCO_3$ and of NaCl. After drying over $MgSO_4$, the solvent was removed by evaporation, followed by silica gel column chromatography (AcOEt : hexane : Et_3N = 90:10:3, $R_f = 0.54$) to afford **6** (0.30 g, yield 91 %). ^{1}H-NMR [$CDCl_3$, 500 MHz] δ = 8.23 (d, J = 9 Hz, 1H), 8.09 (m, 1H), 7.47 (d, J = 9 Hz, 1H), 7.57 (d, J = 9 Hz, 1H), 7.42 (m, 1H), 7.30 (m, 6H), 7.20 (m, 1H), 7.14 (m, 1H), 6.88 (m, 1H), 6.79 (m, 4H), 6.68 (m, 1H), 6.46 (m, 1H), 6.31 (s, 1H), 4.71 (m, 2H), 4.36 (m, 1H), 4.30 (m, 1H), 3.76 and 3.75 (s, 6H), 3.47 (m, 8H), 3.29 (m, 1H), 3.19 (m, 1H), 2.37 (t, J = 6.5 Hz, 2H), 1.27 (m, 10H) , 1.13-0.97 (m, 11H). ^{31}P-NMR [121 MHz, $CDCl_3$] δ =149.5, 147.9. HRMS(FAB) Calcd for $C_{56}H_{64}N_5O_9P$ (M^+) 981.4442. Found 981.4436.

Compound **3** (0.18 g, 0.46 mmol) was coupled with D-threoninol (0.06 g, 0.55 mmol) in the presence of *N*, *N'*-dicyclohexylcarbodiimide (0.11 g, 0.55 mmol) and 1-hydroxybenzotriazole (0.07 g, 0.55 mmol) in DMF. After the reaction mixture was stirred at room temperature for overnight, the solvent was removed and the remained oil was subjected to silica gel column chromatography (CH_3OH : $CHCl_3$ = 1:15, R_f = 0.14) to afford compound **7** (yield 23 %). ^{1}H-NMR [$CDCl_3$, 500 MHz] δ = 7.91 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 2.5 Hz, 1H), 7.46 (d, J = 8 Hz, 1H), 7.28 (d, J = 9 Hz, 1H), 6.94 (dd, J = 8.5 Hz, 2.5 Hz, 1H), 6.46 (dd, J = 9 Hz, 2.5 Hz, 1H), 6.27 (d, J = 2.5 Hz, 1H), 6.05 (s, 1H), 4.58 (m, 2H), 4.42 (br, 1H), 4.30 (m, 1H), 4.09 (br, 1H), 4.01 (m, 2H), 3.97 (m, 1H), 3.39 (q, J = 7 Hz, 4H), 1.29 (d, J = 6.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 6H). ^{13}C-NMR [$CDCl_3$, 126 MHz] δ = 183.1, 168.7, 159.6, 152.2, 151.1, 146.8, 138.6, 133.9, 131.3, 127.9, 126.2, 125.0, 117.7, 110.0, 107.4, 104.7, 96.2, 69.0, 67.6, 65.0, 55.1, 45.3, 20.8, 12.9. HRMS(FAB) Calcd for $C_{26}H_{30}N_3O_6$ ($M+H^+$) 480.2135. Found 480.2144.

1 M. S. J. Briggs, I. Bruce, J. N. Miller, C. J. Moody, A. C. Simmonds and E. Swann, *J. Chem. Soc. Perkin Trans. 1*, 1997, 1051-1058.

2 Y. Hara, T. Fujii, H. Kashida, K. Sekiguchi, X. Liang, K. Niwa, T. Takase, Y. Yoshida and H. Asanuma, *Angew. Chem. Int. Ed.*, 2010, **49**, 5502-5506.

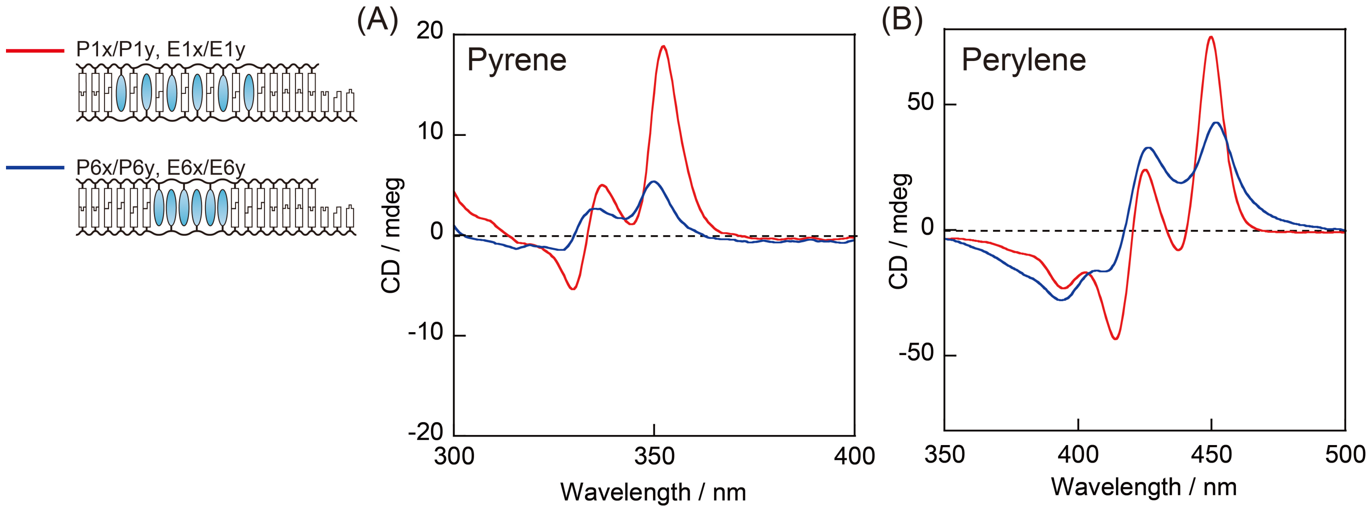


Fig. S1. CD spectra of DNA duplexes containing (A) pyrene or (B) perylene. The CD spectra at 20 °C of (A) **P1x**/**P1y** (red line) and **P6x**/**P6y** (blue line), and (B) **E1x**/**E1y** (red line) and **E6x**/**E6y** (blue line) are shown. Conditions: [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer), [DNA] = 5.0 μM.

Sequences are shown below:

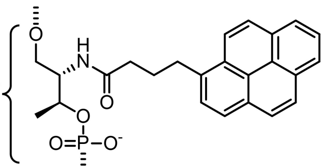
P1x: 5'-GGT**P**TA**P**TT**P**ATGCCG-3'
P1y: 3'-CCAA**P**TA**P**AT**P**ACGGCCTG-5'

E1x: 5'-GGT**E**TA**E**TT**E**ATGCCG-3'
E1y: 3'-CCAA**E**TA**E**AT**E**ACGGCCTG-5'

P6x: 5'-GGTTAT**PPP**TATGCCG-3'
P6y: 3'-CCAATA**PPP**ATACGGCCTG-5'

E6x: 5'-GGTTAT**EEE**TATGCCG-3'
E6y: 3'-CCAATA**EEE**ATACGGCCTG-5'

P



E