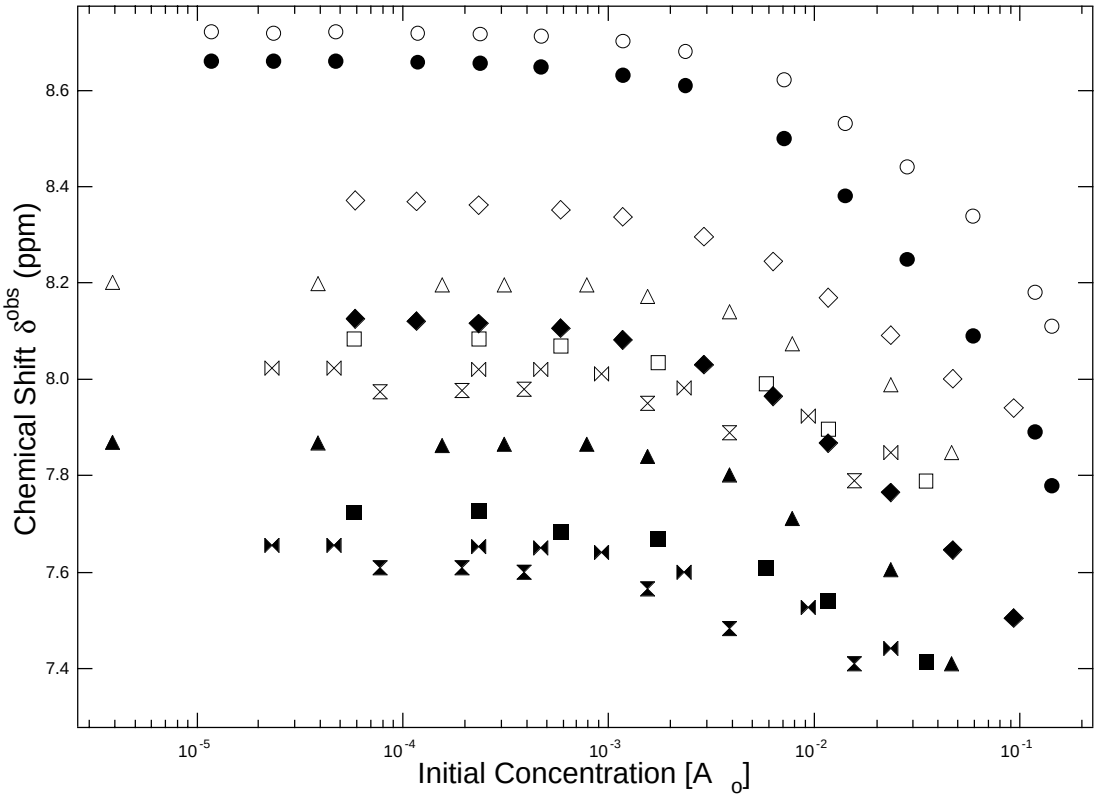


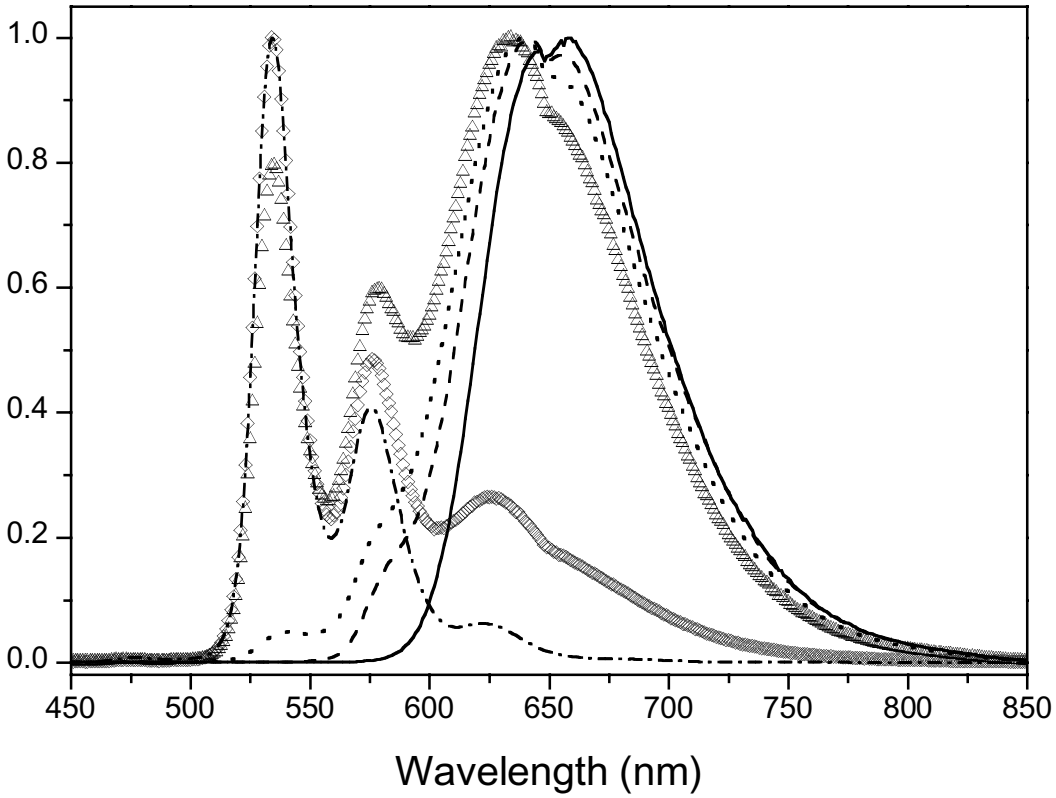
Supporting Information, Figure 1. Observed chemical shifts Ha (open) and Hb (filled) of monomer **1** (circles), dimer **2** (diamonds), trimer **3** (triangles), tetramer **4** (squares), pentamer **5** (horizontal double triangles), and hexamer **6** (vertical double trangles) as a function of the initial molar concentration of each species. Note that the Ha and Hb separation is very small for free monomer in dilute concentrations and is very large for the foldable oligomers 2-6 in dilute concentrations; this effect is caused by the ring current of the π-stacked perylene neighbors.

UV-vis Model for K_{fold}. The equilibrium constant K_{fold} in 1,1,2,2-tetrachloroethane (TCE) was determined by modeling the intensity ratio of the 0→ 0 transition and 0→ 1 transition. The unfolded dimer spectrum was modeled with the free monomer (**1**) at dilute concentration in $CHCl_3$. The folded dimer was modeled with dimer (**2**) in $CHCl_3$, which exist exclusively as the folded structure. The two spectra were then divided by the corresponding concentrations to yield spectra of $\varepsilon_{fold}(\lambda)$ and $\varepsilon_{unfold}(\lambda)$. The observed UV-vis spectra were then fitted to eq. (2) at various temperatures.

$$A^{obs}(\lambda) = C_{fold}\,\varepsilon_{fold}(\lambda) + C_{unfold}\,\varepsilon_{unfold}(\lambda) \qquad (2)$$

The cell thickness is 1 cm and C_{fold} and C_{unfold} are concentrations of the folded and unfolded species, respectively. The equilibrium constant K_{fold} is determined by eq. (3).

$$K_{fold} = C_{fold}/C_{unfold} \qquad (3)$$



Supporting Information, Figure 2. Normalized representative fluorescent spectra of samples along the diagonal direction in Figure 3; this direction yields the largest shift in the optical emissions. All samples were excited at 429 nm using a Xe lamp. The monomeric concentrations of monomer **1** (dash-dot line), dimer **2** (diamonds), trimer **3** (triangles), tetramer **4** (dotted line), pentamer **5** (dashed line), and hexamer **6** (solid line) are 1.6 μM, 6.3 μM, 25 μM, 100 μM, 410 μM, and 1.6 mM. Notice monomer predominately emits green photons, whereas hexamer predominately emits red. The relative quantum yields of monomer **1**, dimer **2**, trimer **3**, tetramer **4**, pentamer **5**, and hexamer **6** measured in dilute concentrations are 100, 74, 42, 30, 30, and 23%, respectively.

Preparation of Monomer (**1**) and foldable Oligomers (**2-6**) based on the foldable blocks of Bis-N, N'-(2-(2-(2-(2-Hydroxy ethoxy) ethoxy) ethoxy) ethyl) perylene tetracarboxylic diimide.

General methods: MALDI Mass Spectra was obtained with an ABVS-2025 spectrometer. Elemental analyses were performed by University of Illinois, Microanalysis Lab, School of Chemical Sciences, 151 Roger Adams Lab, Urbana, IL 61801 USA. ^{1}H NMR spectra were recorded with a Bruker Mercury 300 (300 MHz) spectrometer for solutions in $CDCl_3$ (CD_3OD), $CDCl_2CDCl_2$ or DMSO-d_6 at ambient temperature. ^{13}C NMR spectra were recorded at 75.48 MHz with a Bruker Mercury 300 spectrometer for solutions in DMSO-d_6 adopting 39.50 ppm for the central line of DMSO-d_6 at ambient temperature or $CDCl_3$ (CD_3OD) adopting 77.23 ppm for the central line of $CDCl_3$. ^{31}P NMR chemical shifts are reported in ppm using 85% H_3PO_4 as external reference. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F_{254} (EM Science). Column chromatography was performed on silica gel 60 (230-400 mesh, EM Science).

p-Toluenesulfonic Acid 2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethyl Ester

To a solution of *p*-Toluenesulfonyl chloride (22 g, 0.12 mol) in 200-ml dry CH_2Cl_2 (4A activated MS, 3 days) at 0 ^{o}C, was added tetra(ethylene glycol) (18 ml, 0.10 mol) and dry triethylamine (NaOH, pellets 3 days) (22 ml, 0.16 mol). The reaction mixture was then stirred for 2 h at 0 ^{o}C, and left overnight at room temperature (RT) under argon. Detection of the products on TLC plates was accomplished using UV light or phosphomolybdic acid solution (10% PMA in EtOH). After elimination of the precipitate by filtration, the solution was evaporated under reduced pressure. The residue was purified by chromatography on a silica gel column eluted with EtOAc/Hexane (80:20 to 100:0), and the title product was obtained (12 g, 33% yield) as a colorless oil: R_f 0.2 (EtOAc).

2-[2-[2-(2-Azidoethoxy)ethoxy]ethoxy]ethanol

A solution of monotosyl tetra(ethylene glycol) (6 g, 17.2 mmol) and sodium azide (1.7 g, 26.2 mmol) in 50 ml of acetonitrile was heated under reflux (at 100 ^{o}C of oil bath) for 36 hrs. After return to room temperature, 50 mL of water was added and the mixture was extracted with CH_2Cl_2. Detection of the products on TLC plates was accomplished using sulfuric acid solution (25.0 ml of conc. sulfuric acid, 12.6 g of ammonium molybdate, 0.57 g of cerium sulfate, and 225.0 ml of deionized water). The organic phase was then dried on $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on a silica gel column eluted with EtOAc. The title compound was

obtained as a colorless oil (3.3 g, 89% yield): R_f 0.5 (EtOAc); ^{1}H-NMR ($CDCl_3$) δ3.77-3.59 (m, 14H, CH_2OCH_2, HOCH_2), 3.40 (t, J = 5.0 Hz, 2H, CH_2N$_3$).

2-[2-[2-(2-Aminoethoxy)ethoxy]ethoxy]ethanol

The azido product—2-[2-[2-(2-Azidoethoxy)ethoxy]ethoxy]ethanol (3.3 g, 15.1 mmol), triphenylphosphine (4.4 g, 16.8 mmol), and water (405 mg, 22.5 mmol) were mixed with 20-ml THF. After the solution was stirred for 4 hrs. at room temperature, the solvent was eliminated under reduced pressure and the residual product was purified on a silica gel column that was eluted with $CHCl_3/CH_3OH/Et_3N$ (3:3:1). The title compound was obtained as colorless oil (2.5 g, 86% yield): R_f 0.4 ($CHCl_3/CH_3OH/Et_3N$, 3:3:1). Detection of the products on TLC plates was accomplished using sulfuric acid solution (25.0 ml of conc. sulfuric acid, 12.6 g of ammonium molybdate, 0.57 g of cerium sulfate, and 225.0 ml of deionized water) and/or ninhydrin test solution (a mixture of solution **i**, **ii**, and **iii**: (**i**) 1 ml of 0.1 M aqueous potassium cyanide diluted to 50 ml with pyridine; (**ii**) 2.5 g of ninhydrin in 50 ml of ethanol; (**iii**) 40 g of phenol in 10 ml of ethanol). ^{1}H-NMR ($CDCl_3$) δ3.76-3.51 (m, 14H, CH_2OCH_2, HOCH_2), 2.82 (t, J = 4.9 Hz, 2H, CH_2N).

Bis-N, N'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl)perylenetetracarboxylic diimide (1)

Method A: 2-[2-[2-(2-Aminoethoxy)ethoxy]ethoxy]ethanol (2.6 g, 13.5 mmol), perylenetetracarboxylic dianhydride (2.2 g, 5.6 mmol), and triethylamine (25 ml, 180 mmol) were mixed with 50 ml of dry DMSO (4A activated MS, 3 days) in a 250 ml flask under argon. After the reaction mixture was stirred for 4 h at 150 °C, the reaction solution was cooled to 80 °C and transferred to a 1000 flask. A mixture of 600 ml 10% aqueous HCl and 300 ml methanol was added to the reaction solution, then the solution was stirred for additional 2 hours at 60 °C. After the mixture was cooled to RT overnight, the precipitate was collected using paper filter. The resulting collection was washed with water 400 ml, and the water layer was re-extracted with 50-ml chloroform. The filtrate could be extracted with chloroform to gain more products, but these products are contaminated and need column purification. The combining organic layer was concentrated to give the crude title product; further purification was carried out on a silica gel column that was eluted with CH_2Cl_2/CH_3OH (5:1). Detection of the products on TLC plates was accomplished using UV light or sulfuric acid solution (5% conc. sulfuric acid in EtOH). The title compound was obtained as dark red solid (3.6 g, 86% yield): R_f 0.4 (CH_2Cl_2/CH_3OH, 10:1). ^{1}H-NMR (60-70 mg/0.5 ml; $CDCl_3/CD_3OD$/100/5) δ7.96 (d, 4H, J = 8.1 Hz, aromatic ring), 7.61 (d, 4H, J = 8.1 Hz, aromatic ring), 4.32 (t, 4H, J = 5.7 Hz, CH_2N), 3.65-3.29 (m, 28H, C$H2$OC$H2$, HOCH_2); ^{13}C-NMR (60-70 mg/0.5 ml; $CDCl_3/CD_3OD$/100/5) δ162.7, 133.1, 130.4, 128.1, 124.7, 122.5, 122.4, 72.9, 70.79, 70.76, 70.4, 70.2, 68.0, 61.6, 39.5. ^{1}H-NMR (DMSO-d_6) δ7.13 (bd, 4H, aromatic ring), 6.92 (bd, 4H, aromatic ring), 4.59 (t, 4H, J = 5.7 Hz, CH_2N), 3.65-3.29 (m, 28H, C$H2$OC$H2$, HOCH_2); ^{13}C-NMR (DMSO-d_6) δ161.2, 131.4, 128.8, 125.9, 122.6, 120.2, 72.3, 69.8, 69.7, 69.6, 66.5, 60.2, 45.67. MS (MALDI): m/z 765.82 $[M+Na]^+$. Anal.

Calcd. for $C_{40}H_{42}N_2O_{12}$ (742.77): C 64.68, H 5.70, N 3.77. Found: C 64.24, H 5.52, N 3.83.

Method B: the azido product—2-[2-[2-(2-Azidoethoxy)ethoxy]ethoxy]ethanol (0.5 g, 2.6 mmol) and perylenetetracarboxylic dianhydride (0.4 g, 1.0 mmol) were mixed with 5 ml of dry DMF (4A activated MS, 3 days) in a 25-ml flask under argon. The mixture was heated to 150 ^oC (oil bath 155 ^oC) for 20 hrs. with stirring under argon and cooled to room temperature. The solvent was removed in vacuum and the residue was subject to a silica gel column that was eluted with CH_2Cl_2/CH_3OH (8:1 to 5:1) to give the title product (490 mg, 62% yield), Repeated column purification may be necessary.

Monobenzoylation of Bis-N, N'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl) perylenetetracarboxylic Diimide (1a)

To a solution of bis-N, N'-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl) perylene tetracarboxylic diimide **(1c)** (1.0 g, 1.3 mmol) in pyridine (50 mL) was added BzCl (0.5 mL, 4.3 mmol, ~2.6 eq) dropwise at 0 ^oC under Argon followed by DMAP (~30 mg). The reaction mixture was stirred at RT overnight and TLC (10/0.75, DCM/MeOH) monitoring showed the formation of monosubstituted (Rf 0.4) and disubstituted (Rf 0.75) products as well as the starting material (Rf 0.12). The solvent was removed in vacuum and the residue was diluted by chloroform. The organic phase was washed with water, dried with anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subject to a silica gel column (10/0.75, CH_2Cl_2/MeOH) to give the title product **1a** 248 mg (yield 22.5%) as a red powder. At the same time, disubstituted fraction was also obtained and further monodebenzoylation was carried out as the following: disubstituted compound was dissolved in 20-mL DCM/MeOH (10/1 v/v), then a solution of 2 M MeONa/MeOH was added dropwise to reach pH ~10. After 5 minutes of stirring, Amberlite IR-120 (H^+) was added to quench the reaction (pH~7). The reaction mixture was filtered and the filtrate was collected, concentrated, and subject to a silica gel column (10/0.75, CH_2Cl_2/MeOH) to give the title product **1a** 100 mg (yield 9%), total yield 31.5% based on starting materials **1**. ^1H NMR (25 mg/0.5 ml; $CDCl_3$) δ 8.32 (d, 4H, J = 8.1 Hz, perylene ring), 8.08 (d, 4H, J = 8.1 Hz, perylene ring), 7.98-7.95 (m, 2H, Benzene ring), 7.53-7.48 (m, 1H, Benzene ring), 7.40-7.35 (m, 2H, Benzene ring), 4.45-4.38 (m, 6H, 2CH_2N, CH_2OBz), 3.91-3.56 (m, 26H, C*H2*OC*H2*, HOCH_2); ^{13}C-NMR (60 mg/0.5 ml; $CDCl_3$) δ 166.6, 163.04, 162.99, 133.8, 133.1, 130.9, 130.1, 129.8, 128.8, 128.5, 125.5, 122.95, 122.92, 122.8, 72.8, 71.0, 70.9, 70.6, 70.37, 70.33, 69.4, 68.2, 68.1, 64.39, 62.0, 39.6. MS (MALDI): m/z 847.42 $[M+H]^+$, 869.37 $[M+Na]^+$. Anal. Calcd. for $C_{47}H_{46}N_2O_{13}$ (846.87): C 66.66, H 5.47, N 3.31. Found: C 66.28, H 5.29, N 3.48.

Monotritylation of Bis-N, N'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl) perylenetetracarboxylic Diimide (1c)

2-[2-[2-(2-Aminoethoxy)ethoxy]ethoxy]ethyl)perylenetetracarboxylic diimide **(1)** (730 mg, 0.98 mmol) was dissolved in pyridine 50 mL, followed by addition of DMTrCl (750 mg, 2.22 mmol) and DMAP (~10 mg). The mixture was stirred at RT under argon

overnight, and TLC monitoring (10/0.75, DCM/MeOH) showed the formation of monosubstituted (Rf 0.5) and disubstituted (Rf 0.8) products as well as the starting material (Rf 0.12). The solvent was removed in vacuum and the residue was subject to silica gel column (100/5/1, CH_2Cl_2/MeOH/pyridine) to give the title product **1c** 310 mg (yield 30%) as a red powder. Meanwhile, disubstituted fraction was also collected and further monodetritylation was carried out as the following: A detritylation solution was made by mixing $ZnCl_2$ (1.5 g) into 110 mL of CH_2Cl_2/MeOH (10/1, v/v). Then the disubstituted compound was dissolved by 50 mL of the detritylation solution and the reaction mixture was monitored by TLC (10/0.75, CH_2Cl_2/MeOH). Once the appearance of the spot corresponding to bis-N, N'-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)perylenetetracarboxylic diimide **1** on the TLC plate, the reaction was quenched by pouring into a saturated aq. $NaHCO_3$ solution. The mixture was extracted by chloroform, and the organic layer was washed with brine, collected, concentrated, dried, and subject to silica gel column (100/5/1, CH_2Cl_2/MeOH/pyridine) to give the title product **1c** 180 mg (yield 17.6%), total yield 47.6% based on the starting **1**. The product is stored with a stabilizer diisopropylethylamine under Argon at –80 ^{o}C. ^{1}H NMR ($CDCl_3$) δ 8.39 (d, 4H, J = 8.1 Hz, perylene ring), 8.15 (d, 4H, J = 8.1 Hz, perylene ring), 7.44-7.42 (m, 2H, Benzene ring), 7.32-7.13 (m, 3H, Benzene ring), 7.30 (d, 4H, J = 9.0 Hz, Methoxylbenzene ring), 6,77 (d, 4H, J = 9.0 Hz, Methoxylbenzene ring), 4.48-4.39 (m, 4H, 2CH_2N), 3.91-3.54 (m, 32H, CH_3O, CH_2OCH_2, HOCH_2), 3.17 (t, 2H, J = 5.1 Hz, DMTrOCH_2). Anal. Calcd. for $C_{61}H_{60}N_2O_{14}$ (1045.13): C 70.10, H 5.79, N 2.68. Found: C 69.66, H 5.55, N 3.01.

The Phosphoramidite of Monotritylated Bis-N, N'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl) perylenetetracarboxylic Diimide (1b)

To a solution of monotritylated bis-N, N'-(2-(2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) ethyl) perylenetetracarboxylic diimide **1c** (360 mg, 0.34 mmol) in 25-mL CH_2Cl_2 (dry) was added diisopropylethylamine 0.25 mL (~4eq). Then chloro-N,N-diisopropylaminocyanoethoxyphosphane (0.1 mL, 0.45 mmol, ~1.3 eq) was added dropwise at RT under argon. After 20 min of stirring under argon at RT, the reaction mixture was diluted with CH_2Cl_2 /Et_3N (300/15, v/v) 100 mL and the organic phase was washed with a saturated aq. $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/EtOAc/Et_3N, 3/6/1) to give the title product **1b** 386 mg (yield 90%) as a red powder, which should be used freshly for the next phosphotriester step in order to achieve a higher coupling yield. ^{1}H NMR ($CDCl_3$) δ 8.42 (d, 2H, J = 3.6 Hz, perylene ring), 8.39 (d, 2H, J = 3.6 Hz, perylene ring), 8.19 (d, 2H, J = 3.0 Hz, perylene ring), 8.17 (d, 2H, J = 3.0 Hz, perylene ring), 7.45-7.41 (m, 2H, Benzene ring), 7.30 (dt, 4H, J = 2.4, 9.3 Hz, Methoxylbenzene ring), 7.28-7.12 (m, 3H, Benzene ring), 6.77 (dt, 4H, J = 2.1, 9.0 Hz, Methoxylbenzene ring), 4.44 (bt, 4H, 2CH_2N), 3.89-3.58 (m, 34H, CH_3O, CH_2OCH_2, ((CH$_3$)$_2$CH)$_2$NP(OCH_2CH$_2$CN)(OCH_2), 3.17 (t, 2H, J = 5.1 Hz, DMTrOCH_2), 2.64 (bt, 2H, OCH$_2$CH_2CN), 1.18 (d, 6H, J = 5.4 Hz, (CH_3)$_2$CH). ^{31}P NMR ($CDCl_3$) δ 149.44 (s).

DMTr-Protected Monobenzoylated Dimer (2-DMTr)

The phosphoramidite **1b** (616 mg, 0.5 mmol) and monobenzoylated anchor **1a** (200 mg, 0.24 mmol) were dried at RT in high vacuum for 24 hrs. and dissolved in dry CH_2Cl_2 (30 mL). 3A MS (0.5 g) was added into the solution and the mixture was stirred for 15 min under Argon. Then N-PhIMT (215 mg, 0.73 mmol) was added into the mixture and after 5 hrs. of stirring at RT under argon, a 0.2 M solution of I_2 (5 mL of CH_2Cl_2/Pyridine/H_2O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% $Na_2S_2O_3$ aq. solution and brine, extracted with chloroform. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH/Pyridine, 400/30/2) to give the crude title product **2-DMTr**, which was typically proceeded to the next step—detritylation. ^{1}H NMR ($CDCl_3$) δ 8.16 (d, 4H, J =8.1 Hz, perylene ring), 8.13 (d, 4H, J = 7.8 Hz, perylene ring), 7.89-7.84 (m, 2H, Benzoyl ring), 7.85-7.80 (m, 8H, perylene ring), 7.46-7.13 (m, 8H, Benzoyl and Benzene ring), 7.30 (d, 4H, J = 9.0 Hz, Methoxylbenzene ring), 6.77 (dt, 4H, J = 2.1, 9.0 Hz, methoxylbenzene ring), 4.42-4.20 (m, 16H, 4C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.92-3.56 (m, 54H, C*H*$_3$O, C*H*$_2$OC*H*$_2$), 3.17 (t, 2H, J = 5.1 Hz, DMTrOC*H*$_2$), 2.89 (t, 2H, J = 6.9 Hz, OCH$_2$C*H*$_2$CN).

Monobenzoylated Dimer (2)

The crude **2-DMTr** was dissolved in CH_2Cl_2 30 mL, and 1 mL of $Cl_2CHCOOH$ was added into the solution dropwise at RT. After 10 min of stirring, chloroform was added to dilute the reaction mixture and the organic phase was washed with a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH, 400/30) to give the title product **2** (275 mg, 67% two steps) as a red powder. ^{1}H NMR (10 mg/0.5 ml; $CDCl_3$) δ 8.19 (d, 2H, J = 8.1 Hz, perylene ring), 8.18 (d, 2H, J = 8.1 Hz, perylene ring), 8.15 (d, 2H, J = 8.1 Hz, perylene ring), 8.14 (d, 2H, J = 7.8 Hz, perylene ring), 7.97-7.94 (m, 2H, Benzoyl ring), 7.88-7.82 (m, 8H, perylene ring), 7.53-7.46 (m, 1H, Benzoyl ring), 7.39-7.34 (m, 2H, Benzoyl ring), 4.42-4.20 (m, 16H, 4C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.91-3.56 (m, 50H, C*H*$_2$OC*H*$_2$), 2.89 (t, 2H, J = 6.0 Hz, OCH$_2$C*H*$_2$CN). ^{13}C-NMR (60 mg/0.5 ml; $CDCl_3$) δ 166.6, 162.71, 162.67, 162.64, 133.23, 133.16, 133.14, 130.51, 130.14, 129.77, 128.47, 128.32, 128.27, 124.94, 124.88, 122.64, 122.55, 117.47, 77.52, 72.85, 70.93, 70.89, 70.59, 70.38, 70.34, 70.30, 70.23, 70.15, 69.43, 68.18, 68.15, 68.09, 67.61, 67.53, 64.41, 62.49, 62.42, 61.99, 39.60, 20.01, 19.91. ^{31}P NMR ($CDCl_3$) δ -0.52 (s). MS (MALDI): m/z 1705.33 $[M+H]^+$, 1726.82 $[M+Na]^+$, 1749.39 $[M+2Na-H]^+$.

DMTr-Protected Monobenzoylated Trimer (3-DMTr)

The phosphoramidite **1b** (386 mg, 0.31 mmol) and monobenzoylated dimer **2** (171 mg, 0.1 mmol) were dried at RT in high vacuum for 24 hrs. and dissolved in dry CH_2Cl_2 (30 mL). 3A MS (0.5 g) was added into the solution and the mixture was stirred for 15 min under Argon. Then N-PhIMT (120 mg, 0.34 mmol) was added into the mixture and after

5 hrs of stirring at RT under argon, a 0.2 M solution of I_2 (5 mL of CH_2Cl_2/Pyridine/H_2O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, then filtered and the residue was washed with chloroform. Following the workup procedure described for the synthesis of **2-DMTr**, after the column chromatography, we obtained **3-DMTr**, which was directly proceeded to the next step—detritylation. ^{1}H NMR ($CDCl_3$) δ 8.06-7.92 (m, 14H, perylene ring and benzoyl ring), 7.67-7.63 (m, 8H, perylene ring), 7.55-7.15 (m, 16H, perylene ring, benzene ring, benzoyl ring, methoxylbenzene ring), 6.79-6.75 (m, 4H, methoxylbenzene ring), 4.41-4.20 (m, 26H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.94-3.58 (m, 78H, OC*H*$_3$, C*H*$_2$OC*H*$_2$), 3.18 (t, 2H, J = 5.1 Hz, C*H*$_2$ODMTr), 2.89 (t, 4H, J = 7.0 Hz, OCH$_2$C*H*$_2$CN).

Monobenzoylated Trimer (3)

The crude **3-DMTr** was dissolved in 20-mL CH_2Cl_2, and 0.6-mL of $Cl_2CHCOOH$ was added into the solution dropwise at RT. After 10 min of stirring, chloroform was added to dilute the reaction mixture and the organic phase was washed with a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH, 400/40—400/50) to give the title product **3** (200 mg, 78% two steps) as a red powder. ^{1}H NMR (5 mg/0.5 ml; $CDCl_3$) δ 8.12 (d, 2H, J = 8.1 Hz, perylene ring), 8.11 (d, 2H, J = 8.1 Hz, perylene ring), 8.08 (d, 2H, J = 8.1 Hz, perylene ring), 8.07 (d, 2H, J = 7.8 Hz, perylene ring), 8.03 (2d, 4H, J = 7.8 Hz, perylene ring), 7.97-7.93 (m, 2H, benzoyl ring), 7.79-7.74 (4d, 8H, J = 7.8, 8.1 Hz, perylene ring), 7.66 (bd, 4H, perylene ring), 7.53-7.46 (m, 1H, benzoyl ring), 7.39-7.33 (m, 2H, benzoyl ring), 4.41-4.22 (m, 26H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.92-3.56 (m, 72H, C*H*$_2$OC*H*$_2$), 2.92 (bt, 4H, J = 6.2 Hz, OCH$_2$C*H*$_2$CN). ^{13}C-NMR (35 mg/0.5 ml; $CDCl_3$) δ 166.6, 162.56, 162.54, 162.48, 162.42, 133.14, 133.01, 132.90, 132.76, 130.34, 130.20, 130.14, 129.77, 128.48, 128.11, 128.06, 128.01, 127.90, 124.73, 124.59, 124.45, 122.49, 122.41, 122.38, 122.32, 117.56, 77.53, 72.84, 70.93, 70.89, 70.61, 70.36, 70.25, 70.16, 69.44, 68.11, 67.62, 67.55, 64.41, 62.53, 62.46, 61.99, 39.55, 20.02, 19.93. ^{31}P NMR ($CDCl_3$) δ -0.49 (s). MS (MALDI): m/z 2563.41 $[M+H]^+$, 2584.94 $[M+Na]^+$, 2607.52 $[M+2Na-H]^+$.

DMTr-Protected Monobenzoylated Tetramer (4-DMTr)

The phosphoramidite **1b** (386 mg, 0.31 mmol) and monobenzoylated trimer **3** (166 mg, 0.065 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry DCM (30 mL). 3A MS (0.5 g) was added into the solution and the mixture was stirred for 15 min under argon. Then N-PhIMT (120 mg, 0.34 mmol) was added into the mixture and after 5 hrs. of stirring at RT under argon, a 0.2 M solution of I_2 (5 mL of CH_2Cl_2/pyridine/H_2O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, then filtered and the residue was washed with chloroform. Following the workup procedure described for the synthesis of **2-DMTr**, after the column chromatography, the title product **4-DMTr** was obtained as a crude product, which was directly proceeded to the next step—detritylation. ^{1}H NMR ($CDCl_3$) δ 8.06-7.87 (m, 18H, perylene ring and benzoyl ring), 7.69-7.61 (m, 8H, perylene ring), 7.55-7.15 (m, 20H, perylene ring,

benzene ring, benzoyl ring, methoxylbenzene ring), 6.79-6.75 (m, 4H, methoxylbenzene ring), 4.42-4.15 (m, 36H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.94-3.55 (m, 102H, OC*H*$_3$, C*H*$_2$OC*H*$_2$), 3.18 (t, 2H, J = 5.1 Hz, C*H*$_2$ODMTr), 2.98-2.89 (m, 6H, OCH$_2$C*H*$_2$CN).

Monobenzoylated Tetramer (4)

The crude **4-DMTr** was dissolved in 20-mL CH_2Cl_2, and 0.6 mL of $Cl_2CHCOOH$ was added into the solution dropwise at RT. After 10 min of stirring, chloroform was added to dilute the reaction mixture and the organic phase was washed with a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH, 400/40—400/50) to give the title product **4** (180 mg, 81% two steps) as a red powder. ^{1}H NMR (30 mg/0.5 ml; $CDCl_3$) δ 7.97-7.93 (m, 2H, benzoyl ring), 7.89-7.70 (8d, 16H, J = 7.8 Hz, perylene ring), 7.53-7.20 (m, 19H, benzoyl ring and perylene ring), 4.44-4.14 (m, 36H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.90-3.56 (m, 96H, C*H*$_2$OC*H*$_2$), 2.97-2.89 (3t, 6H, J = 6 Hz, OCH$_2$C*H*$_2$CN). ^{13}C-NMR (30 mg/0.5 ml; $CDCl_3$) δ 166.6, 162.55, 162.51, 162.45, 162.36, 133.14, 132.99, 132.86, 132.66, 130.34, 130.27, 130.14, 129.77, 128.49, 128.11, 128.06, 127.96, 127.82, 124.70, 124.55, 124.36, 124.33, 122.47, 122.38, 122.34, 122.26, 117.63, 117.58, 117.56, 77.52, 72.84, 70.93, 70.89, 70.61, 70.36, 70.26, 70.17, 69.44, 68.10, 67.63, 67.55, 64.41, 62.54, 62.47, 61.99, 39.55, 30.04, 20.03, 19.93. ^{31}P NMR ($CDCl_3$) δ -0.51 (s). MS (MALDI): m/z 3421.98 $[M+H]^+$, 3443.76 $[M+Na]^+$, 3466.17 $[M+2Na-H]^+$.

DMTr-Protected Monobenzoylated Pentamer (5-DMTr)

The phosphoramidite **1b** (290 mg, 0.23 mmol) and monobenzoylated tetramer **4** (100 mg, 0.03 mmol) were dried at RT in high vacuum for 24 hrs. and dissolved in dry CH_2Cl_2 (20 mL). 3A MS (0.5 g) was added into the solution and the mixture was stirred for 15 min under argon. Then N-PhIMT (80 mg, 0.27 mmol) was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I_2 (3 mL of CH_2Cl_2/pyridine/H_2O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, then filtered and the residue was washed with chloroform. Following the workup procedure described for the synthesis of **2-DMTr**, after the column chromatography, **5-DMTr** was obtained as a crude product, which was directly proceeded to the next step—detritylation. ^{1}H NMR ($CDCl_3$) δ 7.96-7.93 (m, 2H, benzoyl ring), 7.88-7.56 (m, 20H, perylene ring), 7.54-7.04 (m, 32H, perylene ring, benzene ring, benzoyl ring, methoxylbenzene ring), 7.76 (d, 4H, J = 8.7 Hz, methoxylbenzene ring), 4.42-4.12 (m, 46H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.86-3.54 (m, 126H, OC*H*$_3$, C*H*$_2$OC*H*$_2$), 3.16 (t, 2H, J = 5.1 Hz, C*H*$_2$ODMTr), 2.96-2.88 (4t, 8H, J = 6 Hz, OCH$_2$C*H*$_2$CN).

Monobenzoylated Pentamer (5)

The crude **5-DMTr** was dissolved in 20-mL CH_2Cl_2, and 0.6 mL of $Cl_2CHCOOH$ was added into the solution dropwise at RT. After 10 min of stirring, chloroform was added to dilute the reaction mixture and the organic phase was washed with a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH, 400/60) to give the pentamer **5** (87 mg, 68% two steps) as a red powder. ^{1}H NMR (20 mg/0.5 ml; $CDCl_3$) δ 7.99-7.95 (m, 2H, benzoyl ring), 7.94-7.79 (4d, 8H, J = 7.8 Hz, perylene ring), 7.78-7.68 (m, 12H, perylene ring), 7.55-7.20 (m, 23H, benzoyl ring and perylene ring), 4.44-4.16 (m, 46H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.90-3.58 (m, 120H, C*H*$_2$OC*H*$_2$), 2.98-2.89 (4t, 8H, J = 6.6 Hz, OCH$_2$C*H*$_2$CN). ^{13}C-NMR (50 mg/0.5 ml; $CDCl_3$/MeOH 10/1 v/v) δ 166.8, 162.62, 162.61, 162.57, 162.51, 162.42, 162.41, 133.18, 133.00, 132.94, 132.89, 132.67, 132.57, 130.34, 130.32, 130.12, 130.11, 129.92, 129.66, 128.45, 127.96, 127.95, 127.94, 127.93, 127.70, 124.61, 124.51, 124.27, 124.17, 122.51, 122.38, 122.28, 122.16, 122.05, 117.54, 117.49, 77.59, 72.82, 70.74, 70.26, 70.10, 70.01, 69.31, 67.94, 67.68, 67.61, 64.37, 62.62, 62.57, 61.50, 39.47, 29.94, 19.86, 19.77. ^{31}P NMR ($CDCl_3$) δ -0.51 (s). MS (MALDI): m/z 4301.80 $[M+Na]^+$, 4323.62 $[M+2Na-H]^+$.

DMTr-Protected Monobenzoylated Hexamer (6-DMTr)

The phosphoramidite **1b** (180 mg, 0.14 mmol) and monobenzoylated pentamer **5** (60 mg, 0.014 mmol) were dried at RT in high vacuum for 24 hrs. and dissolved in dry CH_2Cl_2 (20 mL). 3A MS (0.2 g) was added into the solution and the mixture was stirred for 15 min under argon. Then N-PhIMT (50 mg, 0.17 mmol) was added into the mixture and after 5 h of stirring at RT under argon, a 0.2 M solution of I_2 (2 mL of CH_2Cl_2/pyridine/H_2O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, then filtered and the residue was washed with chloroform. Following the workup procedure described for the synthesis of **2-DMTr**, after the column chromatography, **6-DMTr** was obtained as a crude product, which was directly proceeded to the next step—detritylation. ^{1}H NMR ($CDCl_3$) δ 7.98-7.93 (m, 2H, benzoyl ring), 7.89-7.55 (m, 24H, perylene ring), 7.53-7.45 (m, 1H, benzoyl ring), 7.45-7.04 (m, 35H, perylene ring, benzene ring, benzoyl ring, methoxylbenzene ring), 7.76 (dt, 4H, J = 2.0, 8.7 Hz, methoxylbenzene ring), 4.42-4.12 (m, 56H, C*H*$_2$N, C*H*$_2$OBz, O=P(OC*H*$_2$-)$_2$(OC*H*$_2$CH$_2$CN)), 3.86-3.55 (m, 150H, OC*H*$_3$, C*H*$_2$OC*H*$_2$), 3.16 (t, 2H, J = 5.1 Hz, C*H*$_2$ODMTr), 2.96-2.88 (5t, 10H, J = 6.3 Hz, OCH$_2$C*H*$_2$CN).

Monobenzoylated Hexamer (6)

The crude **6-DMTr** was dissolved in 20-mL CH_2Cl_2, and 0.6 mL of $Cl_2CHCOOH$ was added into the solution dropwise at RT. After 15 min of stirring, chloroform was added to dilute the reaction mixture and the organic phase was washed with a saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH_2Cl_2/MeOH, 400/80) to give hexamer **6** (55 mg, 77% two steps) as a red powder. ^{1}H NMR (10 mg/0.5 ml; $CDCl_3$) δ 7.98-7.94 (m, 2H, benzoyl ring), 7.90-7.73 (4d, 8H, J = 7.8, 8.1 Hz, perylene ring), 7.73-7.61 (m, 16H, perylene ring), 7.55-7.10 (m, 27H, benzoyl ring and perylene ring), 4.43-

4.14 (m, 56H, CH_2N, CH_2OBz, O=P(OCH_2-)$_2$(OCH_2CH$_2$CN)), 3.88-3.54 (m, 144H, CH_2OCH_2), 2.98-2.88 (5t, 10H, J = 6.3 Hz, OCH$_2$CH_2CN). ^{13}C-NMR (40 mg/0.5 ml; $CDCl_3$) δ 166.6, 162.41, 162.39, 162.30, 162.22, 162.20, 133.16, 132.79, 132.58, 132.45, 132.39, 130.14, 129.96, 129.94, 129.77, 128.50, 127.90, 127.70, 127.53, 124.46, 124.20, 124.04, 124.02, 122.30, 122.18, 122.13, 122.05, 122.02, 117.67, 117.63, 117.60, 77.53, 72.90, 70.86, 70.54, 70.31, 70.25, 70.16, 69.43, 68.01, 67.66, 67.58, 64.42, 62.61, 62.54, 61.91, 39.49, 30.03, 20.02, 19.93. ^{31}P NMR ($CDCl_3$) δ -0.54 (s). MS (MALDI): m/z 5158.59 $[M+Na]^+$, 5181.10 $[M+2Na-H]^+$.

Abbreviation:

N-PhIMT: N-Phenyl-imidazolium Triflate

DMAP: 4-Dimethylaminopyridine

DMTrCl: 4,4'-Dimethoxytrityl chloride