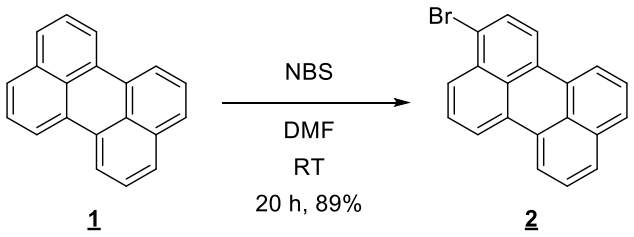
SUPPLEMENTARY METHODS

Solvents, reagents and synthetic procedures

All reactions were carried out under an argon atmosphere unless otherwise specified. Tetrahydrofuran (THF) was distilled from benzophenone ketyl radical under an argon atmosphere. Methanol, dichloromethane (DCM) and diisopropylamine (i-Pr2HN) were distilled from calcium hydride under an argon atmosphere. Acetonitrile (AcCN) was dried over 3Å molecular sieves. Perylene, N-bromosuccinimide (NSB), ethynyltrimethylsilane, tetrabutylammonium fluoride (TBAF) 1.0 M solution in THF, ceric ammonium nitrate (CAN), 4-(dimethylamino)pyridine (DMAP) were purchased from Sigma-Aldrich in ≥ 98% purity, all other solvents or reagents were purified according to literature procedures. ^{1}H-NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; dt, doublet of triplets; t, triplet; td, triplet of doublets; q, quartet; quint, quintet; m, multiplet; and br, broad. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 125 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift. The chemical shifts are reported in parts per million (ppm, δ). The reactions were monitored with a silica gel TLC plate under UV light (254 and 365 nm) followed by visualization with a *p*-anisaldehyde or phosphomolybdic acid staining solution. Column chromatography was performed on silica gel 60, 230-400 mesh. HRMS (ESI) spectra were recorded on Waters LCT premier with ACQUITY LC spectrometer.

Synthesis of the compounds

Bromination reaction for 3-Bromoperylene (2).

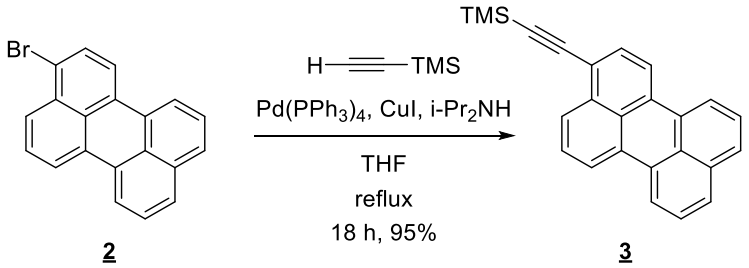


1 2

To perylene 1 (471 mg, 2.0 mmol) in 250 mL-round bottomed flask was added DMF (80 mL) and the mixture was stirred for 1 h until the mixture became a clear solution. Then N-bromosuccinimide (374 mg, 2.1 mmol) solution in DMF (20 mL) was added to the mixture dropwise at room temperature. The reaction mixture was stirred for 20 h at room temperature. After the completion, H_2O was added and stirred for 1 h to generate golden solid, which was collected by filtration. The crude solid (590 mg, 89% yield, golden solid) was assigned to 3-bromoperylene, but it contained small amount of dibromoperylenes by ^1H NMR analysis.

Data for 3-bromoperylene (after recrystallization from toluene): golden solid; ^1H NMR (500 MHz, CDCl3) δ 8.24 (d, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H).

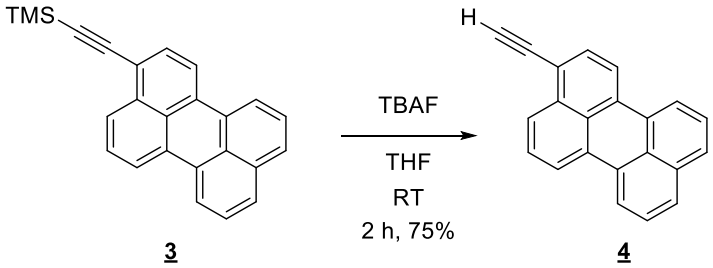
Sonogashira coupling reaction for Trimethyl(perylen-3-ylethynyl)silane (3)



2 **3**

To a THF (5 mL) solution of 3-bromoperylene 2 (83 mg, 0.25 mmol) and tetrakis(triphenylphosphine)-palladium (0) (58 mg, 0.05 mmol) and copper(I) iodide (25 mg, 0.125 mmol) was added diisopropylamine (2.5 ml) at room temperature. The mixture was vigorously stirred for 30 min at 60°C. Then the mixture was added ethynyltrimethylsilane (0.25 mL, 1.75 mmol) and refluxed for 18 h. The mixture was then cooled and diluted with ethyl acetate (50 mL). The organic layer was washed with 3% aq. EDTA solution (3 X 20 mL), sat. aq. NH_4Cl solution (1 X 20 mL) and water (1 X 20 mL), then dried with brine and $MgSO_4$ and concentrated in vacuo. The crude solid (83 mg, 95 %, yellow solid) was assigned to trimethyl(perylen-3-ylethynyl)silane 3 by ^1H NMR analysis: ^1H NMR (500 MHz, DMSO-d_6): δ 8.45 (d, *J* = 7.5 Hz, 1H), 8.41 (d, *J* = 7.5 Hz, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (td, *J* = 8.0, 2.0 Hz, 2H), 0.31 (s, 9H).

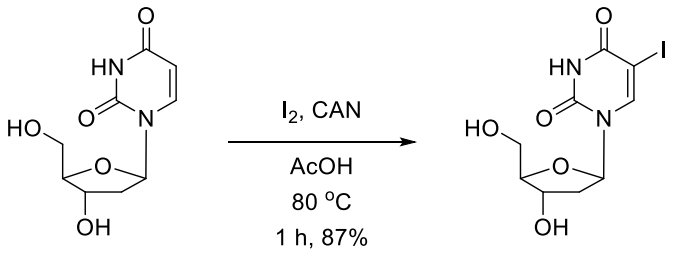
Desilylation reaction for 3-Ethylnylperylene (4)



3 **4**

To a THF (5 mL) solution of trimethyl(perylen-3-ylethynyl)silane **3** (83 mg, 0.25 mmol) was added TBAF 1.0 M solution in THF (0.3 mL, 0.3 mmol) at room temperature. The mixture was stirred for 2 h. The mixture was diluted with ethyl acetate (25 mL) and the organic layer was washed with water (1 X 10 mL), then dried with brine and MgSO4 and concentrated in vacuo. Flash column chromatography (hexanes) afforded the desired product **4** as orange solid (52 mg, 75 %): ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (d, *J* = 6.8 Hz, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.55 (td, *J* = 8.0, 3.2 Hz, 2H), 3.25 (s, 1H).

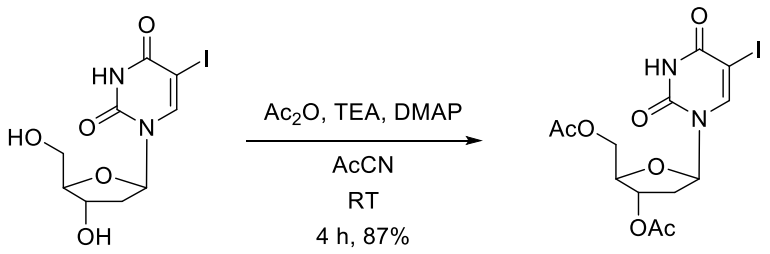
Iodination reaction for 1-((2R, 4S, 5R)-5-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-iodopyrimid-ine-2,4(1H, 3H)-dione (6)



5 **6**

To a mixture of deoxyuridine 5 (114 mg, 0.5 mmol), iodine (92 mg, 0.3 mmol) and ceric ammonium nitrate (137 mg, 0.25 mmol) was added acetic acid (8 mL). The mixture was heated to 80°C and stirred for 1 h. After the iodination was completed, the mixture was evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (only ethyl acetate), and the desired product **6** was obtained as white solid (154 mg, 87 %): ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 8.36 (s, 1H), 6.06 (t, *J* = 6.4 Hz, 1H), 5.20 (d, *J* = 4.4 Hz, 1H), 5.10 (t, *J* = 4.8 Hz, 1H), 4.20 (quint, *J* = 4.4 Hz, 1H), 3.75 (q, *J* = 3.2 Hz, 1H), 3.61-3.52 (m, 2H), 2.10-2.07 (m, 2H).

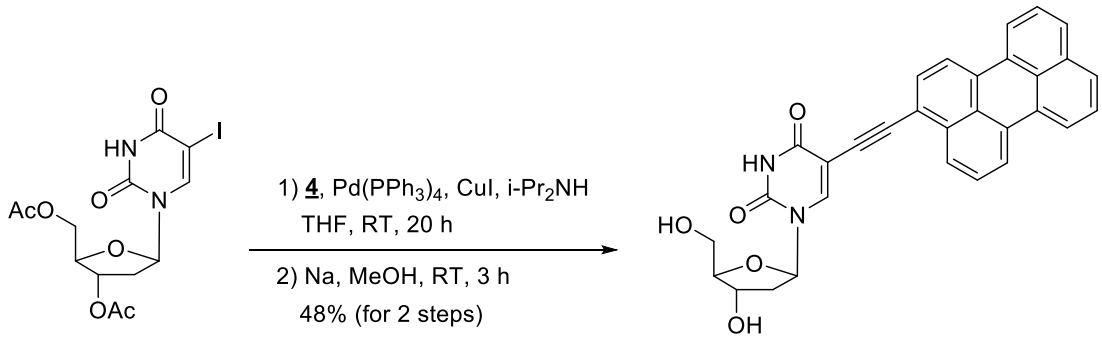
Acetylation reaction for ((2R, 3S, 5R)-3-acetoxy-5-(iodo-3,4-dioxo-3,4-dihydropyrimidine-1(2H)-yl)tetra-hydrofuran-2-yl)methyl acetate (7)



6 **7**

To an acetonitrile (20 mL) solution of **6** (456 mg, 2.0 mmol) and DMAP (24 mg, 0.2 mmol) was added triethylamine (1.12 mL, 8.0 mmol) and acetic anhydride (0.76 mL, 8.0 mmol) at room temperature. The mixture was stirred for 4 h at room temperature. The mixture was diluted with methylene chloride (200 mL) and washed with water (2 X 50 mL), then dried with brine and $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane: ethyl acetate = 1:1), and the desired product **7** was obtained as white solid (76 mg, 87 %): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (br, 1H), 7.97 (s, 1H), 6.28 (dd, *J* = 8.4, 5.6 Hz, 1H), 5.23 (dt, *J* = 6.4, 2.4 Hz, 1H), 4.37 (ddd, *J* = 31.2, 12.4, 3.2 Hz, 2H), 4.31 (m, 1H), 2.54 (ddd, *J* = 14.0, 6.0, 2.0 Hz, 1H), 2.21 (s, 3H), 2.16 (ddd, *J* = 14.0, 6.0, 2.0 Hz, 1H), 2.12 (s, 3H).

Sonogashira coupling reaction and following methanolysis reaction for 1-((2R, 4S, 5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(perylen-3-ylethynyl)pyriidine-2,4-(1H, 3H)-dione (dUY11).



7 dUY11

1) To a THF (5 mL) solution of **7** (75 mg, 0.17 mmol), **4** (47 mg, 0.17 mmol), tetrakis(triphenylphosphine)-palladium (0) (39 mg, 0.034 mmol) and copper(I) iodide (16 mg, 0.085 mmol) was added diisopropylamine (2.5 ml) at room temperature. The mixture was stirred for 20 h. The mixture was diluted with ethyl acetate (50 mL), and the organic layer was washed with 3% aq. EDTA solution (3 X 20 mL), sat. aq. NH_4Cl solution (1 X 20 mL) and water (1 X 20 mL). The organic layer was dried with brine and $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane : ethyl acetate=1:1), and the desired product was obtained as yellow solid (60 mg, 60 %).

2) To a round bottom flask, methanol (10 mL) and Na (7 mg, 0.3 mmol) were added at room temperature. After Na dissolved in methanol completely, a DCM (2 mL) solution of the Sonogashira adduct (60 mg, 0.1 mmol) added to the mixture. The mixture was stirred for 3 h. The mixture was diluted with ethyl acetate (50 mL), and the organic layer was water (1 X 20 mL). The organic layer was dried with brine and $MgSO_4$ and concentrated in vacuo. The

residue was purified by flash column chromatography on silica gel (hexane : ethyl acetate=1:5), and the desired product **dUY11** was obtained as orange solid (40 mg, 80 %): ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.78 (s, 1H), 8.54 (s, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.42 (t, *J* = 7.6 Hz, 2H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 7.84 (dd, *J* = 8.0, 3.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 6.18 (t, *J* = 6.4 Hz, 1H), 5.28 (d, *J* = 4.4 Hz, 1H), 5.24 (t, *J* = 4.8 Hz, 1H), 4.33-4.29 (m, 1H), 3.85 (q, *J* = 3.2 Hz, 1H), 3.74-3.61 (m, 2H), 2.29-2.21 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.0, 149.9, 144.3, 134.7 134.2, 131.6, 131.5, 130.9, 130.6, 130.3, 129.2, 128.9, 128.4, 128.3, 128.1, 127.5, 127.5, 126.3, 122.1, 121.9, 121.8, 120.8, 120.0, 98.8, 91.1, 89.4, 88.1, 85.5, 70.3, 61.3, 29.7 ppm; HRMS calculated for $[C_{31}H_{22}N_2O_5]$+H: 503.1607; Found: 503.1604 $[M+H]^+$.

The overall synthetic scheme to dUY11 is shown below: