**Supplementary Material**

## I. Synthesis of the dendron

### I-I. Preparation of 9-anthrylmethyl N-(3-carboxylpropyl)carbamate (I)

4-Aminobutyric acid (0.50 g, 4.8 mmol, 1.0 equiv) and triehtylamine (TEA) (1.0 ml, 7.3 mmol, 1.5 equiv) were dissolved in N,N-dimethylformamide (DMF) and stirred at 50 $^{o}$C. 9-Anthrylmethyl *p*-nitrophenyl carbonate (1.81 g, 4.8 mmol, 1.0 equiv) was slowly added while stirring. After stirring at 50 $^{o}$C for 2 h, the solution was evaporated to dryness, and the solution was basified with 0.50 N sodium hydroxide (NaOH) solution. The aqueous solution was washed with ethyl acetate (EA), stirred in an ice bath and acidified with dilute hydrochloric acid (HCl). After the product was extracted with EA, the organic solution was dried with anhydrous $MgSO_4$, filtered and evaporated. The total weight of the resulting yellow powder was 1.06 g and the yield was 65 %.

$^{1}$H NMR($CDCl_3$)

δ 11.00-9.00(br, $CH_2COO\mathit{H}$, 1H), 8.41(s, $C_{14}\mathit{H}_9CH_2$, 1H), 8.31(d, $C_{14}\mathit{H}_9CH_2$, 2H), 7.97 (d, $C_{14}\mathit{H}_9CH_2$, 2H), 7.51(t, $C_{14}\mathit{H}_9CH_2$, 2H), 7.46(t, $C_{14}\mathit{H}_9CH_2$, 2H), 6.08(s, $C_{14}H_9C\mathit{H}_2O$, 2H), 5.01(t, $OCON\mathit{H}CH_2$,1H), 3.23(q, $NHC\mathit{H}_2CH_2$, 2H), 2.34(t, $CH_2C\mathit{H}_2COOH$, 2H), 1.77(m, $CH_2C\mathit{H}_2CH_2$, 2H).

$^{13}$C NMR($CDCl_3$)

δ 178.5($CH_2\mathit{C}OOH$), 157.9($O\mathit{C}ONH$), 132.1($\mathit{C}_{14}H_9CH_2$), 131.7($\mathit{C}_{14}H_9CH_2$), 129.7($\mathit{C}_{14}H_9CH_2$), 129.7($\mathit{C}_{14}H_9CH_2$), 127.3($\mathit{C}_{14}H_9CH_2$), 126.8($\mathit{C}_{14}H_9CH_2$), 125.8($\mathit{C}_{14}H_9CH_2$), 124.6($\mathit{C}_{14}H_9CH_2$), 60.2($C_{14}H_9\mathit{C}H_2$), 41.0($NH\mathit{C}H_2CH_2$), 31.7($CH_2\mathit{C}H_2COOH$), 25.6($CH_2\mathit{C}H_2CH_2$).

### I-II. Preparation of 9-anthrylmethyl N-{[(tris{[2-

**(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}propylcarbonate (II)**

9-Anthrylmethyl N-(3-carboxylpropyl)carbamate (0.65 g, 1.93 mmol, 1.5 equiv), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) (0.37 g, 1.93 mmol, 1.5 equiv), and 1-hydroxybenzotriazole hydrate (HOBT) (0.261 g, 1.93 mmol, 1.5 equiv) were dissolved in acetonitrile and stirred at room temperature. Tris{[(methoxycarbonyl)ethoxy]methyl}aminomethane (0.49 g, 1.29 mmol, 1.0 equiv) dissolved in acetonitrile was added with stirring, After stirring at room temperature for 12 h, the acetonitrile was evaporated. The crude product was dissolved in EA and washed with 1.0 N HCl and saturated sodium bicarbonate solution. After being dried with anhydrous $MgSO_4$, filtered, and evaporated, the crude product was loaded in a column packed with silica gel. Purification by column chromatography (eluent: ethyl acetate:haxane = 5:1 (v/v)) resulted in a viscous yellow liquid. The total weight of the yellow liquid was 0.67 g, and the yield was 74 %.

$^1$H NMR($CDCl_3$)

δ 8.43(s, $C_{14}H_9CH_2$, 1H), 8.36(d, $C_{14}H_9CH_2$, 2H), 7.99 (d, $C_{14}H_9CH_2$, 2H), 7.53(t, $C_{14}H_9CH_2$, 2H), 7.47(t, $C_{14}H_9CH_2$, 2H), 6.15(s, CONHC, 1H), 6.08(s, $C_{14}H_9CH_2O$, 2H), 5.44(t, OCONHCH$_2$,1H), 3.63-3.55(m, $CH_2OCH_2CH_2COOCH_3$, 21H), 3.27(q, NHCH$_2$CH$_2$, 2H), 2.46(t, CH$_2$CH$_2$COOCH$_3$, 6H), 2.46(t, CH$_2$CH$_2$CONH, 2H), 1.81(m, CH$_2$CH$_2$CH$_2$, 2H).

$^{13}$C NMR($CDCl_3$)

δ 173.2($CH_2CONH$), 172.7($CH_2COOCH_3$), 157.4(OCONH), 132.9($C_{14}H_9CH_2$), 131.5($C_{14}H_9CH_2$), 129.5($C_{14}H_9CH_2$), 129.4($C_{14}H_9CH_2$), 127.5($C_{14}H_9CH_2$), 127.0($C_{14}H_9CH_2$), 125.6($C_{14}H_9CH_2$), 124.7($C_{14}H_9CH_2$), 69.6(NHC$CH_2$O), 67.2($C_{14}H_9CH_2$), 60.1(O$CH_2CH_2$), 59.4(NH$CCH_2$), 52.1(O$CH_3$), 40.8(NH$CH_2CH_2$),

35.1($OCH_2CH_2$), 34.7($CH_2CH_2CONH$), 26.3($CH_2CH_2CH_2$).

Anal. Calcd for $C_{36}H_{46}N_2O_{12} \cdot 0.5\ H_2O$: C 61.18, H 6.65, N 4.03; Found: C 61.09, H 6.69, N 3.96.

**I-III. Preparation of 9-anthrylmethyl N-[({tris[(2-carboxyethoxy)methyl]methyl}amino)carbonyl]propylcarbamate (III)**

9-Anthrylmethyl N-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}propylcarbonate (0.67 g, 0.93 mmol) was dissolved in acetone (30 ml) and 0.20 N NaOH (30 ml, 6 mmol). After being stirred at room temperature for 1 d, the acetone was evaporated. The aqueous solution was washed with EA, stirred in an ice bath and acidified with dilute HCl. After the product was extracted with EA, the organic solution was dried with anhydrous $MgSO_4$, filtered and evaporated. Solidification in acetone and ether solution at -20 $^oC$ resulted in a yellow powder. The total weight of the final pale yellow powder was 0.54 g with a yield of 88 %.

$^1H$ NMR($CDCl_3$)

δ 11.00-9.00(br, $CH_2COO\mathit{H}$, 3H), 8.61(s, $C_{14}\mathit{H}_9CH_2$, 1H), 8.47(d, $C_{14}\mathit{H}_9CH_2$, 2H), 8.11 (d, $C_{14}\mathit{H}_9CH_2$, 2H), 7.60(t, $C_{14}\mathit{H}_9CH_2$, 2H), 7.52(t, $C_{14}\mathit{H}_9CH_2$, 2H), 6.63(s, CON$\mathit{H}$C, 1H), 6.36(t, OCON$\mathit{H}CH_2$, 1H), 6.12(s, $C_{14}H_9C\mathit{H}_2O$, 2H), 3.40-3.63(m, $C\mathit{H}_2OC\mathit{H}_2CH_2COOH$, 12H), 3.20(q, $NHC\mathit{H}_2CH_2$, 2H), 2.52(t, $CH_2C\mathit{H}_2COOH$, 6H), 2.17(t, $CH_2C\mathit{H}_2CONH$, 2H), 1.75(m, $CH_2C\mathit{H}_2CH_2$, 2H).

$^{13}C$ NMR($CDCl_3$)

δ 172.2($CH_2\mathit{C}OOH$), 172.0($CH_2\mathit{C}ONH$), 156.7(O$\mathit{C}$ONH), 131.2($\mathit{C}_{14}H_9CH_2$), 130.7($\mathit{C}_{14}H_9CH_2$), 128.6($\mathit{C}_{14}H_9CH_2$), 128.4($\mathit{C}_{14}H_9CH_2$), 127.3($\mathit{C}_{14}H_9CH_2$), 126.2($\mathit{C}_{14}H_9CH_2$), 124.8($\mathit{C}_{14}H_9CH_2$), 124.0($\mathit{C}_{14}H_9CH_2$), 68.6(NHC$\mathit{C}H_2O$),

66.5($C_{14}H_9CH_2$), 59.5($OCH_2CH_2$), 58.0($NHCCH_2$), 40.0($NHCH_2CH_2$), 34.0($OCH_2CH_2$), 33.5($CH_2CH_2CONH$), 25.8($CH_2CH_2CH_2$).

Anal. Calcd for $C_{33}H_{40}N_2O_{12} \cdot 1.5\ H_2O$: C 57.97, H 6.34, N 4.10; Found: C 57.89, H 6.21, N 4.09.

**I-IV. Preparation of 9-anthrylmethyl N-[({tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]methyl}amino)carbonyl]propylcarbamate (IV)**

9-Anthrylmethyl N-[({tris[(2-carboxyethoxy)methyl]methyl}amino)carbonyl]propylcarbamate (0.54 g, 0.82 mmol, 1.0 equiv), EDC (0.55 g, 2.87 mmol, 3.5 equiv), and HOBT (0.39 g, 2.89 mmol, 3.5 equiv) were dissolved in acetonitrile and stirred at room temperature. Tris{[(methoxycarbonyl)ethoxy]methyl}aminomethane (0.96 g, 2.53 mmol, 3.1 equiv) dissolved in acetonitrile was added with stirring, After stirring at room temperature for 36 h, the acetonitrile was evaporated. The crude product was dissolved in EA and washed with 1.0 N HCl and saturated sodium bicarbonate solution. After drying with anhydrous $MgSO_4$, filtered, and evaporated, the crude product was loaded in a column packed with silica gel. Column purification (eluent: ethyl acetate:methanol = 20:1 (v/v)) resulted in a viscous yellow liquid. The total weight of the yellow liquid was 1.26 g with an 88 % yield.

$^1$H NMR($CDCl_3$)

δ 8.47(s, $C_{14}H_9CH_2$, 1H), 8.39(d, $C_{14}H_9CH_2$, 2H), 8.02 (d, $C_{14}H_9CH_2$, 2H), 7.53(t, $C_{14}H_9CH_2$, 2H), 7.47(t, $C_{14}H_9CH_2$, 2H), 6.60(s, $CH_2CH_2CH_2CONHC$, 1H), 6.13(s, $OCH_2CH_2CONHC$, 3H), 6.11(s, $C_{14}H_9CH_2O$, 2H), 5.79(t, $OCONHCH_2$,1H), 3.65-3.60(m, $CH_2OCH_2CH_2CONH$, $CH_2OCH_2CH_2COOCH_3$, 75H), 3.29(q, $NHCH_2CH_2$, 2H),

2.50(t, $CH_2CH_2COOCH_3$, 18H), 2.36(t, $OCH_2CH_2CONH$, 6H), 2.27(t, $CH_2CH_2CH_2CONH$, 2H), 1.85(m, $CH_2CH_2CH_2$, 2H).

$^{13}$C NMR($CDCl_3$)

δ 173.3($OCH_2CH_2CONH$), 172.5($CH_2CH_2CH_2CONH$), 171.6($CH_2COOCH_3$), 157.2(OCONH), 131.8($C_{14}H_9CH_2$), 131.5($C_{14}H_9CH_2$), 129.4($C_{14}H_9CH_2$), 129.3($C_{14}H_9CH_2$), 127.6($C_{14}H_9CH_2$), 127.0($C_{14}H_9CH_2$), 125.6($C_{14}H_9CH_2$), 124.7($C_{14}H_9CH_2$), 69.5($NHCCH_2OCH_2CH_2COOCH_3$), 67.9($NHCCH_2OCH_2CH_2CONH$), 67.2($C_{14}H_9CH_2$), 60.3($OCH_2CH_2CONH$), 60.2($OCH_2CH_2COOCH_3$), 59.2($NHCCH_2OCH_2CH_2COOCH_3$, $NHCCH_2OCH_2CH_2CONH$), 52.1($OCH_3$), 41.0($NHCH_2CH_2$), 37.6($OCH_2CH_2CONH$), 35.1($OCH_2CH_2COOCH_3$), 34.7($CH_2CH_2CH_2CONH$), 26.3($CH_2CH_2CH_2$).

Anal. Calcd for $C_{81}H_{121}N_5O_{36} \cdot H_2O$: C 55.31, H 7.05, N 3.98; Found: C 55.05, H 7.08, N 4.04.

MALDI-TOF-MS: 1763.2 (MNa+), 1779.2 (MK+).

**I-V. Preparation of 9-anthrylmethyl N-({[tris({2-[({tris[(2-carboxyethoxy)methyl]methyl}amino)carbonyl]ethoxy}methyl)methyl]amino}carbonyl)propylcarbamate (V)**

9-Anthrylmethyl N-[({tris[(2-{[(tris{[2-(methoxycarbonyl)ethoxy]methyl}methyl)amino]carbonyl}ethoxy)methyl]methyl}amino)carbonyl]propylcarbamate (0.60 g, 0.34 mmol) was dissolved in acetone (30 ml) and 0.20 N NaOH (30 ml). After stirring at room temperature for 1 d, the acetone was evaporated. The aqueous solution was washed with EA, stirred in an ice bath and acidified with dilute HCl. After the product was extracted with EA, the organic solution was dried with anhydrous $MgSO_4$, filtered and evaporated. The total weight of the final

yellow powder was 0.37 g and the yield was 68 %.

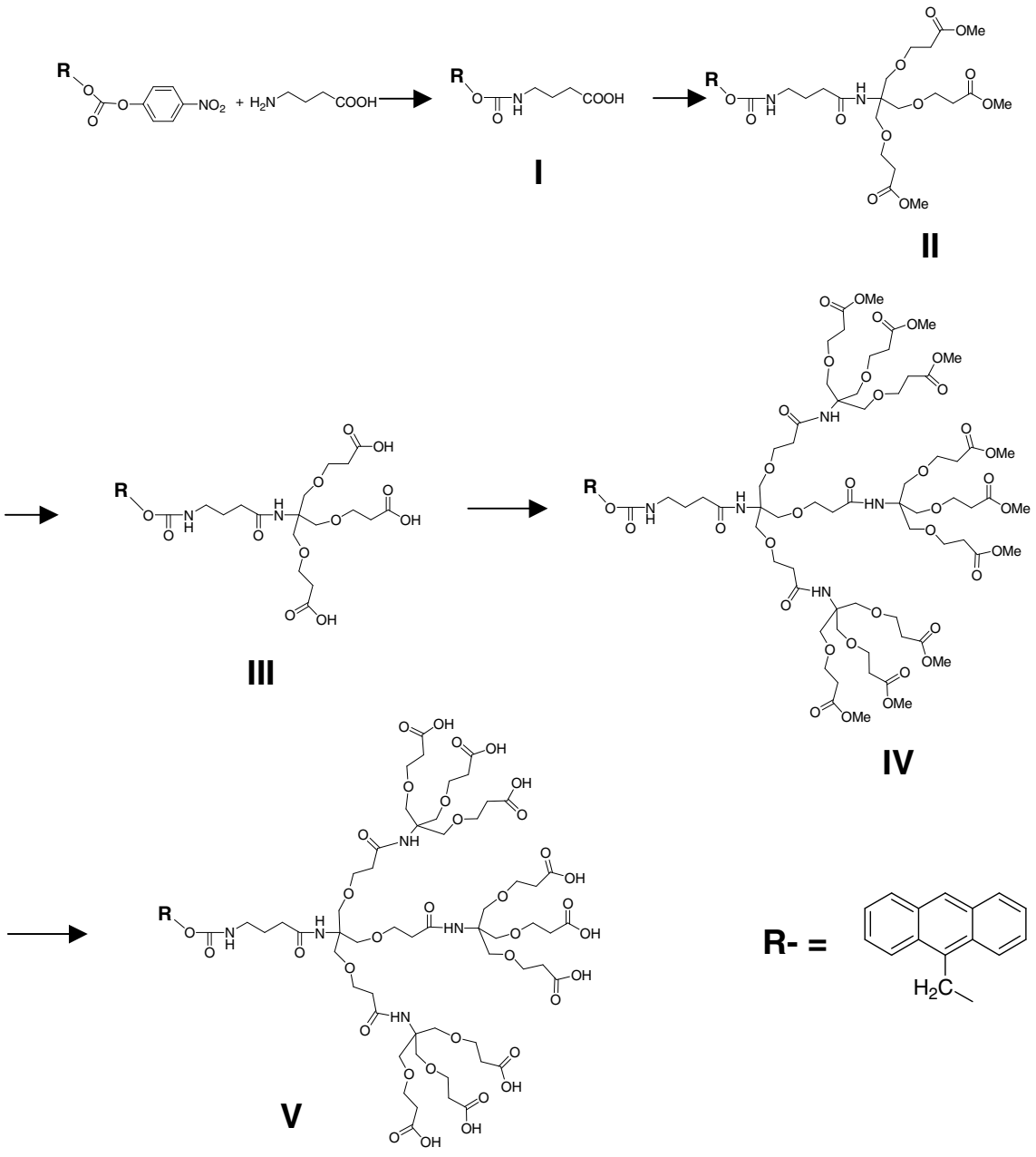
$^{1}$H NMR(DMSO)

δ 13.00-11.00(br, $CH_2COOH$, 9H), 8.66(s, $C_{14}H_9CH_2$, 1H), 8.42(d, $C_{14}H_9CH_2$, 2H), 8.13 (d, $C_{14}H_9CH_2$, 2H), 7.62(t, $C_{14}H_9CH_2$, 2H), 7.54(t, $C_{14}H_9CH_2$, 2H), 7.12(t, $OCONHCH_2$, 1H), 7.10(s, $OCH_2CH_2CONHC$, 3H), 7.06(s, $CH_2CH_2CH_2CONHC$, 1H), 6.06(s, $C_{14}H_9CH_2O$, 2H), 3.57-3.55(m, $CH_2OCH_2CH_2CONH$, $CH_2OCH_2CH_2COOH$, 48H), 3.02(q, $NHCH_2CH_2$, 2H), 2.42(t, $CH_2CH_2COOH$, 18H), 2.32(t, $OCH_2CH_2CONH$, 6H), 2.11(t, $CH_2CH_2CH_2CONH$, 2H), 1.60(m, $CH_2CH_2CH_2$, 2H).

$^{13}$C NMR(DMSO)

δ 172.8($CH_2COOH$), 172.2($CH_2CH_2CH_2CONH$), 170.5($OCH_2CH_2CONH$), 156.5($OCONH$), 131.0($C_{14}H_9CH_2$), 130.6($C_{14}H_9CH_2$), 129.0($C_{14}H_9CH_2$), 128.7($C_{14}H_9CH_2$), 127.6($C_{14}H_9CH_2$), 126.7($C_{14}H_9CH_2$), 125.4($C_{14}H_9CH_2$), 124.3($C_{14}H_9CH_2$), 68.3($NHCCH_2OCH_2CH_2COOH$), 67.4($NHCCH_2OCH_2CH_2CONH$), 66.8($C_{14}H_9CH_2$), 59.8($OCH_2CH_2COOH$), 59.6($OCH_2CH_2CONH$), 57.9($NHCCH_2OCH_2CH_2CONH$), 55.9($NHCCH_2OCH_2CH_2COOH$), 36.4($NHCH_2CH_2$), 34.6($OCH_2CH_2COOH$), 30.8($OCH_2CH_2CONH$), 29.7($CH_2CH_2CH_2CONH$), 25.9($CH_2CH_2CH_2$).

## II. Synthetic scheme



**III. Preparing the dendron-modified substrates**

**Cleaning the substrates.** Substrates such as oxidized silicon wafer, fused silica, and glass slide, were immersed into Piranha solution (conc. $H_2SO_4$:30% $H_2O_2$ = 7:3 (v/v)), and the reaction bottle containing the solution and the substrates was sonicated for an hour. (Caution: Piranha solution can oxidize organic materials explosively. Avoid contact with oxidizable materials.) The plates were washed and rinsed thoroughly with a copious amount of deionized water after the sonication. The clean substrates were dried in a vacuum chamber (30-40 mTorr) for the next steps.

**Preparing the hydroxylated substrates.** The above clean substrates were soaked in anhydrous toluene solution with 50 mM (3-glycidoxypropyl)methyldiethoxysilane (GPDES) for 10 h. After the self-assembly, the substrates were washed with toluene briefly, placed in an oven, and heated at 110 $^{o}$C for 30 min. The plates were sonicated in toluene, toluene-methanol (1:1 (v/v)), and methanol in a sequential manner for 3 min at each washing step. The washed plates were dried in a vacuum chamber (30-40 mTorr). GPDES-modified substrates were soaked in a neat ethylene glycol (EG) solution with one or two drops of 95 % sulfuric acid at 90 $^{o}$C for 8 h. After cooling, the substrates were sonicated in ethanol and methanol in a sequential manner each for 3 min. The washed plates were dried in a vacuum chamber (30-40 mTorr).

**Preparing the dendron-modified substrates.** The above hydroxylated substrates were immersed into a methylene chloride solution with a small amount of DMF dissolving the dendron (1 mM) and a coupling agent, 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) or 1,3-dicyclohexylcarbodiimide (DCC) (9.3 mM) in the presence of 4-dimethylaminopyridine (DMAP) (0.9 mM). After 1 day at room temperature, the plates were sonicated in methanol, water, and methanol in a

sequential manner each for 3 min. The washed plates were dried in a vacuum chamber (30-40 mTorr) for the next step.

**Preparing the NHS-modified substrates.** The dendron-modified substrates were immersed into a methylene chloride solution with 1.0 M trifluoroacetic acid (TFA). After 3 h, they were again soaked in a methylene chloride solution with 20 % (v/v) diisopropylethylamine (DIPEA) for 10 min. The plates were sonicated in methylene chloride and methanol each for 3 min. After being dried in a vacuum chamber, the deprotected substrates were incubated in the acetonitrile solution with di(N-succinimidyl)carbonate (DSC) (25 mM) and DIPEA (1 mM). After 4 h reaction under nitrogen atmosphere, the plates were placed in a stirred dimethylformamide solution for 30 min and washed briefly with methanol. The washed plates were dried in a vacuum chamber (30-40 mTorr) for the next step.

**IV. Hybridization intensity and discrimination efficiency depending on linkers on the silanated slide**

PDITC and DSC linkers were utilized to investigate the effect of linkers on hybridization intensity and discrimination efficiency on the silanated slide. Figure S1 and Table S1 showed that PDITC linker gave stronger signal than DSC linker did, while discrimination ratios are almost constant. Because the former intensity is as large as that of DSC/dendron case, we compared both cases in the main text. In addition, it was found that nonspecific binding of non-complementary target DNAs on both slides was insignificant.

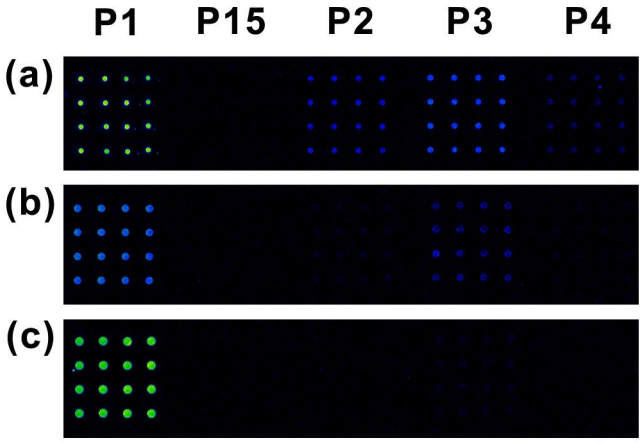



**Figure S1.** Fluorescence images after the hybridization with T1 target oligonucleotide on (a) a silanated slide modified with a PDITC linker, (b) a silanated slide modified with a DSC linker, and (c) a dendron slide modified with a DSC linker. P1 represents the case where a probe oligonucleotide complementary with the target oligonucleotide (T1) was employed; P15 represents the case with a non-complementary probe; P2-P4

represent the cases with a single internal mismatched probe. Laser power and PMT gain of a laser scanner were adjusted to record the reasonable signals of mismatched pairs while avoiding saturation of the signal of the matched one.

**Table S1.** Fluorescence intensity and discrimination ratio after hybridization with the target oligonucleotide (T1).

| | | P1 | P15 | P2 | P3 | P4 |
|---|---|---|---|---|---|---|
| PDITC linker / | Fluorescence Intensity | 24293 | 17 | 2312 | 5194 | 1020 |
| Silanated slide | Discrimination Ratio | 100 | 0.1 | 9.6 | 21.5 | 4.2 |
| DSC linker / | Fluorescence Intensity | 6691 | 20 | 442 | 1318 | 241 |
| Silanated slide | Discrimination Ratio | 100 | 0.3 | 6.6 | 19.7 | 3.6 |
| DSC linker / | Fluorescence Intensity | 22067 | 12 | 23 | 177 | 15 |
| Dendron slide | Discrimination Ratio | 100 | 0.1 | 0.1 | 0.8 | 0.1 |