Supporting Information

Highly Selective Recognition of Adenine Nucleobase by Synthetic Hosts with Linked Five-Six-Five-Membered Triheteroaromatic Structure and the Application to Potentiometric Sensing of Adenine Nucleotide


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I. Synthesis and Characterization of Compounds

Synthesis of Reference 3

Scheme S1. Synthesis of host 1 (and reference 3). a) DPPA (2.5 eq), Et$_3$N, DMF, RT, 20 h; then 1-hexanol, DMF, 100 °C, 2 h; 1 (41%) and 3 (22%).

Other Preparative Method for 1 (and 3): Compound 1 was also prepared by employing the reported procedure using diphenylphosphoryl azide (DPPA). To a stirred solution of 10 (120 mg, 0.4 mmol) in DMF (5 mL) was added successively Et$_3$N (350 mg, 3.5 mmol) and DPPA (550 mg, 2 mmol) in one portion, respectively, at RT under N$_2$ atmosphere. After stirred for 20 h, 1-hexanol (10 mL) was added and the reaction mixture was heated at 100 °C for 2 h. The resulting solution was diluted with CHCl$_3$ (90 mL), and the organic layer was washed successively with 5%aq citric acid (25 mL), satd aq NaHCO$_3$ (25 mL) and brine (25 mL). The aqueous layers were extracted again with CHCl$_3$ (25 mL), and the extract was washed with brine (25 mL). The combined organic layers were dried over anhyd MgSO$_4$, filtered and evaporated. The residue was purified by column chromatography (alumina, CHCl$_3$-hexane = 1:1) to give 1 (white solid, 82 mg, 41%), together with 3 (white solid, 41 mg, 22%).

2,2’-(Pyridine-2,6-diyl)bis(oxazole-4-carboxylic acid) Dihexyl Ester (3): mp 117-119 °C (recrystallized from EtOH). $^1$H-NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 0.91 (t, $^3$J(H,H) = 7.0 Hz, 6 H; CH$_3$), 1.26-1.47 (m, 12 H; (CH$_2$)$_3$CH$_2$), 1.79 (quin, $^3$J(H,H) = 6.8 Hz, 4 H; OCH$_2$CH$_2$), 4.38 (t, $^3$J(H,H) = 6.8 Hz, 4 H; OCH$_2$), 0.83 (t, $^3$J(H,H) = 7.6 Hz, 1 H; PyH(parac)), 8.40 (s, 2 H; CH of oxazole), 8.43 (d, $^3$J(H,H) = 7.6 Hz, 2 H; PyH(meta)) ppm. $^{13}$C-NMR (125 MHz, CDCl$_3$, TMS): $\delta$ = 14.0, 22.5, 25.5, 28.6, 31.4, 45.66, 51.44, 134.9, 138.3, 145.0, 145.5, 160.2, 161.0 ppm. IR (KBr): $\nu_{max}$ = 1730 cm$^{-1}$ (νC=O, ester). MS (El, 70 eV): m/z (%): 469 (100) [M$^+$], 386 (69), 302 (73), 190 (82). Elemental analyses calcld (%) for C$_{25}$H$_{31}$N$_2$O$_6$: C 63.95, H 6.65, N 8.95; found: C 63.90, H 6.54, N 9.17.
Synthesis of Reference 4

Scheme S2. Synthesis of reference 4. a) SOCl₂, reflux, 21 h. b) l-SerOMe·HCl, Et₃N, CHCl₃, RT, 1 d, 27% from isophthalic acid. c) Et₂NSF₃, CH₂Cl₂, -78 °C, 4 h; then K₂CO₃, -78 °C → RT, overnight; 84%. d) BrCCl₃, DBU, CH₂Cl₂, 0 °C, overnight, 89%. e) KOH, MeOH-H₂O, RT, 3 h then reflux, 1.5 h, 90%. f) SOCl₂, reflux, overnight. g) NaN₃, acetone-H₂O, 0 °C, 1 h → RT, 4.5 h. h) CHCl₃, reflux, 3 h; then 1-hexanol, CHCl₃, reflux, overnight; 16% from 18.

N,N’-(Phenylene-1,3-diylidicarbonyl)bis-l-serine Dimethyl Ester (15): This compound was obtained from isophthalic acid (3.01 g, 18.1 mmol) by the procedures similar as those for 7. After purification by column chromatography (silica gel, AcOEt-MeOH = 5:1), the desired product 15 was obtained as a white solid (1.81 g, 27%): mp 152-154 °C (recrystallized from AcOEt). ¹H-NMR (500 MHz, CDCl₃, TMS): δ = 3.85 (s, 6 H; CH₃), 4.09-4.17 (m, 4 H; CH₂), 4.88 (m, 2H; CH), 7.39 (t, 3J(H,H) = 7.9 Hz, 1 H; C-5 CH of benzene), 7.51 (d, 3J(H,H) = 7.6 Hz, 1 H; NH), 7.90 (d, 3J(H,H) = 7.9 Hz, 2 H; C-4.6 CH of benzene), 8.25 (s, 1 H; C-2 CH of benzene) ppm. ¹³C-NMR (125 MHz, CDCl₃, TMS): δ = 53.0, 55.4, 63.2, 125.2, 129.2, 131.0, 133.6, 166.7, 171.2 ppm. IR (KBr): νmax = 3370 (νOH), 1750 and 1740 (νC=O, ester), 1645 and 1635 (νC=O, amide) cm⁻¹. MS (FAB): m/z: 369 [M+H]+. Elemental analyses calc'd (%) for C₁₉H₂₀N₂O₆: C 52.17, H 5.47, N 7.61; found: C 52.26, H 5.54, N 7.75.

(S,S)-2,2’-(1,3-Phenylene)bis(4,5-dihydroxazole-4-carboxylic acid) Dimethyl Ester (16): This compound was obtained from 15 (2.27 g, 6.16 mmol) by the procedures similar as those for 8. After purification by column chromatography (silica gel, CHCl₃-MeOH = 30:1), the desired product 16 was obtained as a white solid (1.72 g, 84%): mp 129-130 °C (recrystallized from AcOEt). ¹H-NMR (500 MHz, CDCl₃, TMS): δ = 3.83 (s, 6 H; CH₃), 4.61 (dd, 3J(H,H) = 10.7, 3J(H,H) = 8.5 Hz, 2 H; one of CH₂), 4.71 (br dd, 3J(H,H) = 8 Hz, 2 H; CH), 4.97 (dd, 3J(H,H) = 10.7, 3J(H,H) = 7.9 Hz, 2 H; one of CH₂), 7.48 (t, 3J(H,H) = 7.9 Hz, 1 H; C-5 CH of benzene), 8.13 (d, 3J(H,H) = 7.9 Hz, 2 H; C-4.6 CH of benzene), 8.56 (s, 1 H; C-2 CH of benzene) ppm. ¹³C-NMR (125 MHz, CDCl₃, TMS): δ = 52.8, 68.7, 69.7, 127.4, 128.6, 128.8, 131.9, 165.5, 171.4 ppm. IR (KBr): νmax 1740 and 1726 cm⁻¹(νC=O, ester). MS (FAB): m/z: 333 [M+H]+.
2,2’-(1,3-Phenylene)bis(oxazole-4-carboxylic acid) Dimethyl Ester (17): This compound was obtained from 16 (1.28 g, 3.85 mmol) by the procedures similar as those for 9. After purification by column chromatography (silica gel, CHCl₃), the desired product 17 was obtained as a white solid (1.12 g, 89\%): mp 194-196 °C (recrystallized from AcOEt). ¹H-NMR (500 MHz, CDCl₃, TMS): δ = 3.98 (s, 6 H; CH₃), 7.61 (t, ³J(H,H) = 7.9 Hz, 1 H; C-5 CH of benzene), 8.27 (d, ³J(H,H) = 7.9 Hz, 2 H; C-4.6 CH of benzene), 8.34 (s, 2 H; CH of oxazole), 8.84 (s, 1 H; C-2 CH of benzene) ppm. ¹³C-NMR (125 MHz, CDCl₃, TMS): δ = 52.3, 125.1, 127.3, 129.4, 129.6, 134.7, 144.1, 161.5, 161.6 ppm. IR (KBr): νₘₐₓ = 1740 and 1730 cm⁻¹ (νC=O, ester). MS (FAB): m/z: 329 [M+H]⁺. Elemental analyses calcd (%) for C₁₅H₁₂N₂O₆: C 58.54, H 3.68, N 8.53; found: C 58.35, H 3.87, N 8.12.

2,2’-(1,3-Phenylene)bis(oxazole-4-carboxylic acid) (18): This compound was obtained from 17 (0.30 g, 5.5 mmol) by the procedures similar as those for 14, yielding the desired product 18 as a white solid (0.248 g, 90\%): mp 276-287 °C (recrystallized from CHCl₃/MeOH). ¹H-NMR (500 MHz, [D₆]DMSO, TMS): δ = 7.79 (t, ³J(H,H) = 7.9 Hz, 1 H; C-5 CH of benzene), 8.19 (d, ³J(H,H) = 7.9 Hz, 2 H; C-4.6 CH of benzene), 8.60 (s, 1 H; C-2 CH of benzene), 8.92 (s, 2 H; CH of oxazole), 13.25 (br s, 2 H; COOH) ppm. ¹³C-NMR (125 MHz, CDCl₃, TMS): δ = 123.8, 127.1, 128.5, 130.5, 134.6, 145.8, 160.2, 161.8 ppm. IR (KBr): νₘₐₓ = 3600–3200 (νOH, carboxy), 1695 (νC=O, ester) cm⁻¹. MS (FAB): m/z: 307 [M+H]⁺.

2,2’-(1,3-Phenylene)bis(oxazole-4-carboxylic acid) Diethyl Ester (4): This compound was obtained from 18 (0.400 g, 1.33 mmol) by the procedures similar as those for 1. After purification by column chromatography (alumina, CHCl₃-hexane = 1:10), the desired product 4 was obtained as a white solid (0.094 g, 16\%): mp 155-156 °C (recrystallized from AcOEt). ¹H-NMR (500 MHz, CDCl₃, TMS): δ = 0.89 (t, ³J(H,H) = 6.7 Hz, 6 H; CH₃), 1.31 (m, 12 H; (CH₂₃)CH₂), 1.66 (m, 4 H; OCH₂CH₂), 4.18 (m, 4 H; OCH₂), 7.05 (br s, 2 H; NH), 7.54 (t, ³J(H,H) = 7.9 Hz, 1 H; C-5 CH of benzene), 7.91 (s, 2 H; CH of oxazole), 8.04 (d, ³J(H,H) = 7.9 Hz, 2 H; C-4.6 CH of benzene), 8.59 (s, 1 H; C-2 CH of benzene) ppm. ¹³C-NMR (125 MHz, CDCl₃, TMS): δ = 14.0, 22.5, 25.5, 28.8, 31.4, 66.1, 124.0, 124.6, 127.8, 129.4, 138.3, 153.1, 158.3 ppm. IR (KBr): νₘₐₓ = 3300, 3150 (νNH, carbamoyl), 1710 (νC=O, carbamoyl) cm⁻¹. MS (FAB): m/z: 499 [M+H]⁺. Elemental analyses calcd (%) for C₂₀H₁₄N₂O₆: C 62.70, H 6.88, N 11.25; found: C 62.40, H 6.82, N 11.48.
**Synthesis of Lipophilic Nucleoside Guests.** A series of lipophilic nucleoside guests, applicable in organic solvents, were prepared, introducing tert-butylidimethylsilyl groups to all hydroxy groups by the reported procedure\[^{82-84}\] with some modifications.

![Nucleoside guests](attachment:image.png)

**Scheme S3.** Lipophilic nucleoside guests.

**2',3',5'-Tris-O-(tert-butylidimethylsilyl)adenosine (5A):** This compound was prepared from adenosine and tert-butylidimethylsilyl chloride (TBDMSCl) with imidazole in anhyd DMF by employing the reported procedure\[^{83}\] with some modifications. After purification by column chromatography (silica gel, AcOEt-hexane = 1:3), the desired product 5A was obtained as a white solid (1.84 g, 75%): mp 143-144 °C (recrystallized from hexane) [lit.: mp 142-144 °C\[^{82b}\]]. \(^1\)H-NMR (400 MHz, CDCl₃, TMS): δ = -0.23, -0.04, 0.10, 0.11, 0.13 and 0.14 (six s, each 3 H; SiCH₃ × 6), 0.80, 0.93 and 0.96 (three s, each 9 H; C(CH₃)₃ × 3), 3.79 (dd, \(^3\)J(H,H) = 11.5, \(^3\)J(H,H) = 2.9 Hz, 1 H; one of C-5’ CH₂), 4.03 (dd, \(^3\)J(H,H) = 11.5, \(^3\)J(H,H) = 4.4 Hz, 1 H; one of C-5’ CH₂), 4.13 (ddd, \(^3\)J(H,H) = 2.9, 3.9, 4.4 Hz, 1 H; C-4’ CH₂), 4.32 (dd, \(^3\)J(H,H) = 3.9, 4.8 Hz, 1 H; C-3’ CH₃), 4.69 (dd, \(^3\)J(H,H) = 4.8, 5.4 Hz, 1 H; C-2’ CH₂), 5.50 (s, 2 H; NH₂), 6.03 (d, \(^3\)J(H,H) = 5.4 Hz, 1 H; C-1’ CH₂), 8.16 (s, 1 H; C-8 CH), 8.34 (s, 1 H; C-2 CH) ppm. HRMS (ESI) calcd (m/z) for C₂₉H₄₅N₅O₄Si₃ [M+H]: 610.3640. Found: 610.3631. Elemental analyses calcd (%) for C₂₉H₄₅N₅O₄Si₃: C 55.13, H 9.09, N 11.48; found: C 54.91, H 8.94, N 11.32.

**2',3',5'-Tris-O-(tert-butylidimethylsilyl)guanosine (5G):** This compound was prepared from guanosine and TBDMSCl with imidazole in anhyd DMF by employing the reported procedure\[^{83}\] with some modifications. After purification by column chromatography (silica gel, AcOEt-hexane = 1:1), the desired product 5G was obtained as a white solid (3.300 g, 53%): mp 288-290 °C (recrystallized from hexane) [lit.: > 300 °C (dec),\[^{83}\] mp > 245 °C\[^{83}\]]. \(^1\)H-NMR (400 MHz, CDCl₃, TMS): δ = -0.06, 0.01, 0.09, 0.10, 0.13 and 0.14 (six s, each 3 H; SiCH₃ × 6), 0.86, 0.93 and 0.96
(three s, each 9 H; C(CH$_3$)$_3$ × 3), 3.78 (dd, $^2$J(H,H) = 11.5, $^3$J(H,H) = 2.4 Hz, 1 H; one of C-5′ CH$_2$), 3.98 (1 H; m, one of C-5′ CH$_2$), 4.10 (m, 1 H; C-4′ CH), 4.28 (t, $^3$J(H,H) = 4.4 Hz, 1 H; C-3′ CH), 4.35 (m, 1 H; C-2′ CH), 5.83 (d, $^3$J(H,H) = 4.4 Hz, 1 H; C-1′ CH), 5.97 (br s, 2 H; NH$_2$), 7.90 (s, 1 H; C-8 CH), 12.10 (br s, 1 H; NH ppm). Elemental analyses calcld (%) for C$_{28}$H$_{55}$N$_5$O$_5$Si$_3$: C 53.72, H 8.86, N 11.19; found: C 53.51, H 8.86, N 11.06.

**2′,3′,5′-Tris-O-(tert-butyl(dimethyl)silyl)cytidine (5C):** This compound was prepared from cytidine and TBDMSCI with pyridine, triethylamine and AgNO$_3$ in THF by employing the reported procedure$^{[54]}$ with some modifications. After purification by column chromatography (silica gel, CHCl$_3$:MeOH = 50:1), the desired product 5C was obtained as a white solid (2.81 g, 96%): mp 125-126 °C (recrystallized from hexane) [lit.: mp 103-109 °C$^{[55]}$]. 1H-NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 0.04 and 0.05 (two s, each 3 H; SiCH$_3$ × 2), 0.12 (s, 6 H; SiCH$_3$ × 2), 0.14 and 0.24 (two s, each 3 H; SiCH$_3$ × 2), 0.88, 0.91 and 0.95 (three s, each 9 H; C(CH$_3$)$_3$ × 3), 3.77 (br d, $^2$J(H,H) = 10.5 Hz, 1 H; one of C-5′ CH$_2$), 4.01-4.12 (m, 4 H; C-2′, C-3′ and C-4′ CH plus one of C-5′ CH$_2$), 5.58 (d, $^3$J(H,H) = 7.3 Hz, 1 H; C-5 CH), 5.78 (d, $^3$J(H,H) = 1.5 Hz, 1 H; C-1′ CH), 8.21 (d, $^3$J(H,H) = 7.3 Hz, 1 H; C-6 CH) ppm. MS (ESI): m/z: 586 [M+H]+. Elemental analyses calcld (%) for C$_{28}$H$_{55}$N$_5$O$_5$Si$_3$: C 55.34, H 9.46, N 7.17; found: C 55.19, H 9.43, N 7.31.

**2′,3′,5′-Tris-O-(tert-butyl(dimethyl)silyl)uridine (5U):** This compound was prepared from uridine and TBDMSCI with imidazole in anhyd DMF by employing the reported procedure$^{[52b,53]}$ with some modifications. After purification by column chromatography (silica gel, AcOEt-hexane = 1:3), the desired product 5U was obtained as a white hard gum$^{[52b]}$ (2.13 g, 73%). 1H-NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 0.06, 0.07, 0.08, 0.09, 0.12 and 0.13 (six s, each 3 H; SiCH$_3$ × 6), 0.89, 0.91 and 0.95 (three s, each 9 H; C(CH$_3$)$_3$ × 3), 3.75 (br d, $^2$J(H,H) = 11.5 Hz, 1 H; one of C-5′ CH$_2$), 3.98 (br d, $^2$J(H,H) = 11.5 Hz, 1 H; one of C-5′ CH$_2$), 4.07-4.09 (m, 3 H; C-2′, C-3′ and C-4′ CH), 5.67 (dd, $^3$J(H,H) = 3.7, 8.0 Hz, 1 H; C-5 CH), 5.88 (d, $^3$J(H,H) = 3.7 Hz, 1 H; C-1′ CH), 8.01 (d, $^3$J(H,H) = 8.0 Hz, 1 H; C-6 CH), 8.08 (br s, 1 H; NH ppm). MS (FAB): m/z: 587 [M+H]+. Elemental analyses calcld (%) for C$_{27}$H$_{53}$N$_5$O$_5$Si$_3$: C 55.25, H 9.27, N 4.77; found: C 54.99, H 9.46, N 4.71.

**3′,5′-Bis-O-(tert-butyl(dimethyl)silyl)thymidine (6T):** This compound was prepared from thymidine and TBDMSCI with imidazole in anhyd DMF by employing the reported procedure.$^{[52b,53]}$ After purification by column chromatography (silica gel, AcOEt-hexane = 1:3), the desired product 6T was obtained as a white solid (2.16 g, 92%): mp 144-145 °C$^{[52a]}$ (recrystallized from hexane) [lit.: mp 144-145 °C$^{[52a]}$]. 1H-NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 0.077 and 0.084 (two s, each 3 H; SiCH$_3$ × 2), 0.12 (s, 6 H; SiCH$_3$ × 2), 0.90 and 0.93 (two s, each 9 H; C(CH$_3$)$_3$ × 2), 1.92 (s, 3 H; ArCH$_3$), 2.00 (m, 1 H; one of C-2′ CH$_2$), 2.25 (m, 1 H; one of C-2′ CH$_2$), 3.76 (dd, $^2$J(H,H) = 11.7, $^3$J(H,H) = 2.4 Hz, 1 H; one of C-5′ CH$_2$), 3.87 (dd, $^2$J(H,H) = 11.7, $^3$J(H,H) = 2.4 Hz, 1 H; one of C-5′ CH$_2$), 3.94 (m, 1 H; C-4′ CH), 4.41 (m, 1 H; C-3′ CH), 6.33 (dd, $^3$J(H,H) = 5.9, 8.1 Hz, 1 H; C-1′ CH), 7.47 (s, 1 H; C-6 CH), 7.95 (br s, 1 H; NH ppm). MS (FAB): m/z: 471 [M+H]+. Elementary analyses calcld (%) for C$_{28}$H$_{55}$N$_5$O$_5$Si$_3$: C 56.13, H 8.99, N 5.95; found: C 56.27, H 9.21, N 6.21.
II. $^1$H-NMR Measurements

![Job's Plot](image)

**Figure S1.** Job’s plot for the complex of host 1 and guest 5A, obtained by $^1$H-NMR measurements (400 MHz) in CDCl$_3$ at 27 °C. [Host 1]$_0$ + [Guest 5A]$_0$ = 10.0 mM; solvent, CDCl$_3$; temperature, 27 °C. The concentration of the host-guest complex ([HG]) was estimated from $\Delta \delta_{\text{obsd}}$ for the NHCO$_2$CH$_2$ signal of host 1, according to the equation, $[\text{HG}] = (\delta_{\text{obsd}} - \delta_{\text{H}})[\text{H}]_0 / (\delta_{\text{HG}} - \delta_{\text{H}})$.

![1H-NMR spectra](image)

**Figure S2.** $^1$H-NMR spectra (400 MHz) of reference 3 and/or guest 5A in CDCl$_3$. [Reference 3]$_0$ = 0 or 20 mM; [guest 5A]$_0$ = 0 or 20 mM. Measured at 23 °C, using CHCl$_3$ as the internal standard ($\delta$ = 7.26 ppm).

Negligible changes in the chemical shifts of both host and guest indicate negligible host-guest complexation.
Figure S3. $^1$H-NMR spectra (500 MHz) of reference 4 and/or guest 5A in CDCl$_3$. [Reference 4]$_0$ = 0 or 10 mM; [guest 5A]$_0$ = 0, 10 or 20 mM. Measured at ca. 25 °C using TMS as the external standard.

A moderate degree of host-guest complexation by hydrogen bonding is supported by guest-induced downfield shift of the carbamoyl NH signal of the host (purple arrows) and also by host-induced downfield shift of the NH$_2$ signal of the guest (blue arrows).

### III. Fluorescence Measurements

![Fluorescence spectrum](image)

Figure S4. Fluorescence spectra of reference 3 in the presence of nucleoside guests (5A, 5G, 5C, 5U or 6T). [Reference 3]$_0$ = 20 μM; [guest 5A, 5G, 5C, 5U or 6T]$_0$ = 200 μM. $\lambda_{ex}$ = 320 nm;
solvent, CHCl₃; temperature, 20 °C. The ordinate indicates relative fluorescence intensity.

Guest-induced change of the fluorescence of host 3 is negligible in the presence of a large excess of the guest, indicating negligible host-guest complexation.

**Determination of the Stability Constants of Host-Guest Complexes:**

Stability constants of 1:1 complexes ($K_s$ [M⁻¹]) were determined by the Benesi-Hildebrand analysis using the KaleidaGraph program. The condition: [1] = 20 μM, [5A] = 240–580 μM, [5G, 5C, 5U, or 5T] = 4.0–16.0 mM. [2] = 20 μM, [5A] = 240–580 μM, [5C] = 0.80–1.6 mM, [5G, 5U, or 5T] = 4.0–16.0 mM. [4] = 20 μM, [5A] = 2.0–12.0 mM. Fluorescence emission at 380 nm (host 1), 371 nm (host 2) or 376 nm (reference 4) was measured in CHCl₃ at 20 °C with excitation at 336 nm (host 1 with all guests), 326 nm (host 2 with all guests) or 312 nm (reference 4 with guest 5A).

![Hildebrand-Benesis Analysis](image)

**Hildebrand-Benesis Analysis**

\[
1/\Delta F = 1/(K_s \cdot \Delta F_{\text{max}})((1/[G]_0) + (1/\Delta F_{\text{max}}))
\]

\[
1/\Delta F = 9.46 \times 10^{-8} (1/[G]_0) + 1.17 \times 10^{-3}
\]

Stability Constant

$K_s = 12400 \pm 600$ M⁻¹

(CHCl₃, 20 °C)

correlation coefficient R = 0.99

[Host 1]₀ = 20 μM

[Guest 5A]₀ = 240–580 μM

solvent: CHCl₃; temperature 20 °C

**Figure S5.** Determination of stability constant ($K_s$ [M⁻¹]) for the 1:1 complex of host 1 and guest 5A from the fluorescence intensity changes (380 nm).
**Figure S6.** Determination of stability constant ($K$, [M⁻¹]) for the 1:1 complex of host 1 and guest 5G from the fluorescence intensity changes (380 nm).

**Figure S7.** Determination of stability constant ($K$, [M⁻¹]) for the 1:1 complex of host 1 and guest 5C from the fluorescence intensity changes (380 nm).
Figure S8. Determination of stability constant ($K$, [M$^{-1}$]) for the 1:1 complex of host 1 and guest 6T from the fluorescence intensity changes (380 nm).

Hildebrand-Benessi Analysis

\[
1/\Delta F = 1/(K_s \cdot \Delta F_{\text{max}})((1/[G]_0 + (1/\Delta F_{\text{max}})
\]

\[1/\Delta F = 1.75 \times 10^{-7} (1/[G]_0) + 1.85 \times 10^{-3}\]

Stability Constant

$K_s = 10500 \pm 400$ M$^{-1}$

(CHCl$_3$, 20 °C)

Correlation coefficient R = 0.99

[Host 2]$_0$ = 20 μM

[Guest 5A]$_0$ = 240 ~ 580 M

Solvent: CHCl$_3$; Temperature 20 °C

Figure S9. Determination of stability constant ($K$, [M$^{-1}$]) for the 1:1 complex of host 2 and guest 5A from the fluorescence intensity changes (371 nm).

Hildebrand-Benessi Analysis

\[
1/\Delta F = 1/(K_s \cdot \Delta F_{\text{max}})((1/[G]_0 + (1/\Delta F_{\text{max}})
\]

\[1/\Delta F = 4.41 \times 10^{-5} (1/[G]_0) + 2.71 \times 10^{-3}\]

Stability Constant

$K_s = 62 \pm 8$ M$^{-1}$

(CHCl$_3$, 20 °C)

Correlation coefficient R = 0.99

[Host 2]$_0$ = 20 μM

[Guest 5G]$_0$ = 4.0 ~ 16.0 mM

Solvent: CHCl$_3$; Temperature 20 °C

Figure S10. Determination of stability constant ($K$, [M$^{-1}$]) for the 1:1 complex of host 2 and guest 5G from the fluorescence intensity changes (371 nm).
Hildebrand-Benesi Analysis
\[
1/\Delta F = \left[ \frac{1}{K_s \cdot \Delta F_{\text{max}}} \right] \left[ \frac{1}{[G]_0} \right] + \left( \frac{1}{\Delta F_{\text{max}}} \right)
\]

\[1/\Delta F = 6.97 \times 10^{-6} \left( \frac{1}{[G]_0} \right) + 1.14 \times 10^{-3}\]

Stability Constant

\[K_s = 163 \pm 40 \text{ M}^{-1}\]

(CHCl₃, 20 °C)

Correlation coefficient \(R = 0.99\)

[Host 2]₀ = 20 μM

[Guest 5C]₀ = 0.80 ~ 1.6 mM

Solvent: CHCl₃; temperature 20 °C

**Figure S11.** Determination of stability constant \((K_s [\text{M}^{-1}])\) for the 1:1 complex of host 2 and guest 5C from the fluorescence intensity changes (371 nm).

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Hildebrand-Benesi Analysis
\[
1/\Delta F = \left[ \frac{1}{K_s \cdot \Delta F_{\text{max}}} \right] \left[ \frac{1}{[G]_0} \right] + \left( \frac{1}{\Delta F_{\text{max}}} \right)
\]

\[1/\Delta F = 2.49 \times 10^{-4} \left( \frac{1}{[G]_0} \right) + 6.66 \times 10^{-3}\]

Stability Constant

\[K_s = 27 \pm 16 \text{ M}^{-1}\]

(CHCl₃, 20 °C)

Correlation coefficient \(R = 0.99\)

[Host 2]₀ = 20 μM

[Guest 6T]₀ = 4.0 ~ 16.0 mM

Solvent: CHCl₃; temperature 20 °C

**Figure S12.** Determination of stability constant \((K_s [\text{M}^{-1}])\) for the 1:1 complex of host 2 and guest 6T from the fluorescence intensity changes (371 nm).
**Hildebrand-Benesi Analysis**

\[
1/\Delta F = \left[1/(K_s \cdot \Delta F_{\text{max}})\right] \left(1/[G]_0\right) + \left(1/\Delta F_{\text{max}}\right)
\]

\[
1/\Delta F = 2.11 \times 10^5 \left(1/[G]_0\right) + 3.35 \times 10^{-3}
\]

Stability Constant

\[K_s = 159 \pm 22 \, \text{M}^{-1}\]

(CHCl₃, 20 °C)

correlation coefficient R = 0.99

[Host 4]₀ = 20 µM

[Guest 5A]₀ = 2.0 ~ 12.0 mM

solvent: CHCl₃; temperature 20 °C

---

**Figure S13.** Determination of stability constant (\(K_s [\text{M}^{-1}]\)) for the 1:1 complex of reference 4 and guest 5A from the fluorescence intensity changes (376 nm).

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**IV. UV-Vis Spectrophotometric Measurements**

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**Figure S14.** UV-Vis absorption spectra of host 1 with increasing concentration of adenosine guest 5A. The condition: \([1] = 60 \, \mu\text{M}, [5A] = 60\sim 480 \, \mu\text{M}; \text{solvent, CHCl}_3; \text{temperature, 20 °C.}\)
Figure S15. Determination of stability constant ($K_a [M^{-1}]$) for the 1:1 complex of host 1 and guest 5A from the absorbance changes (350 nm) by the nonlinear least-square curve fitting method using the KaleidaGraph program.

V. Calculation of the Optimized Structure and Energy of Host-Guest Complex

Model Complex of Host 1’ (R = CH₃) and 9-Methyladenine. The optimized structure was obtained by the non-empirical molecular orbital calculation (see footnote 18 of the text).

![Structural diagram](image)

1: R = -(CH₂)₅CH₃
1’: R = -CH₃
**Figure S16.** The optimized structure of the model complex of host 1’ (R = CH₃) and 9-methyladenine.

Top view: The N-H···N distances in the model complex of host 1’ and 9-methyladenine (2.06, 1.90, 2.04 and 1.97 Å from left to right), which are much shorter than the van der Waals distance (ca. 2.4 Å), suggest the formation of four hydrogen bonds (blue lines) with adenine nucleobase in the complex by host 1. On the other hand, the distances between the pyridine nitrogen of host 1’ and the NH₂ hydrogens of the guest is found to be much longer (2.92 and 2.69 Å), indicating that the pyridine nitrogen in host 1 does not contribute as a hydrogen bonding acceptor. Lateral view: Completely planar structure of the host-guest complex.
Table S1. Atomic coordinates for the optimized structure of the model complex of host $\mathbf{1}'$ (R = CH$_3$) and 9-methyladenine.$^{[a]}$

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[a] B3LYP/6-31G* optimized cartesian coordinates are listed. The total electronic energy (HF) was calculated to be -1811.2211576 hartree.
VI. Potentiometric Measurements

Reagents: The following compounds were of the highest grade commercially available and used without further purification: Tridodecylmethylammonium chloride (TDDMACl; catalog number 91661) and poly(vinyl chloride) (PVC, high molecular weight; 81392) from Fluka (Buchs, Switzerland);  
o-nitrophenyl octyl ether (NPOE; 347-04522) from Dojindo Laboratories (Kumamoto, Japan);  
adenosine 5’-monophosphate (5’-AMP, disodium salt; 302-50743) and cytidine 5’- 
monophosphate (5’-CMP, disodium salt; 030-05363) from Wako Pure Chemical (Osaka, Japan);  
guanosine 5’-monophosphate (5’-GMP, disodium salt; G-8377) and uridine 5’-monophosphate (5’- 
UMP, disodium salt; U-6375 from Sigma-Aldrich (St. Louis, USA).