

## Supporting Information for

### G-octamer Scaffold via Self-assembly of Guanosine-based Au(I) Isonitrile Complex for Au(I)-Au(I) Interaction

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#### General Methods.

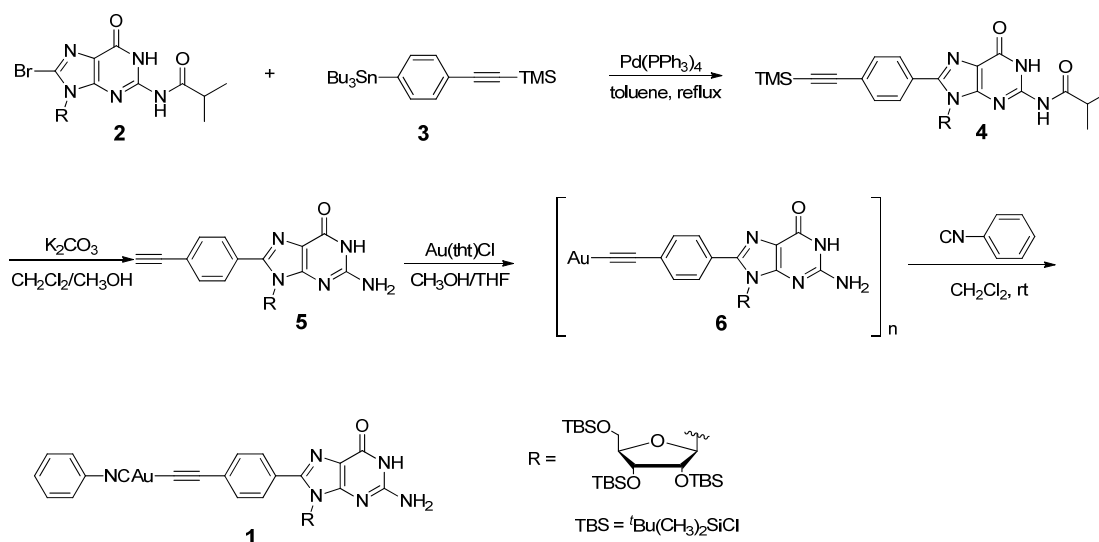
All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Solvents employed were dried by refluxing in the presence of appropriate drying reagents and distilled under nitrogen. Analytical thin-layer chromatography (TLC) was performed on Merck TLC plate (silica gel 60 F254, 0.25 mm). Column chromatography was conducted on silica gel (Wakogel C-200). NMR spectra were recorded on a JNM-ECS 400 (400 MHz) and a Varian Unity INOVA 600 (600 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-700 or JMS-T100LC equipped with CSI source.

#### Physical Measurements.

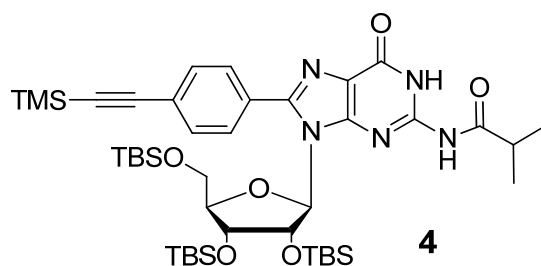
UV/vis spectra were obtained using a Hitachi U-3500 spectrophotometer in chloroform solution with the concentration  $3.0 \times 10^{-4}$  M under argon at 298 K. UV-vis spectra were

measured using 1 mm pathlength quartz cuvettes. Emission spectra were collected using a Shimadzu RF-5300PC spectrofluorophotometer in chloroform solution with the concentration  $3.0 \times 10^{-4}$  M under argon at 298 K. Emission spectra were measured using 5 mm pathlength quartz cuvettes. CD spectra of **1** were recorded using a JASCO J-720 spectropolarimeter in chloroform solution with the concentration  $3.0 \times 10^{-4}$  M under argon at 298 K. CD spectra were measured using 5 mm pathlength quartz cuvettes.

### Preparation of the Au(I) Complex **1**.



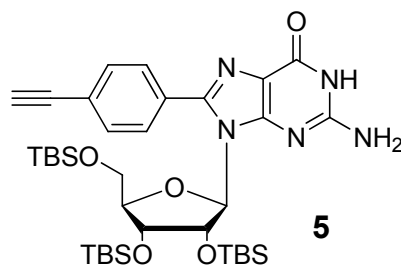
Scheme S1. Synthesis of **1**



A solution of **2** (368 mg, 0.47 mmol) and **3** (660 mg, 1.42 mmol) in dry toluene (20 ml) was purged with nitrogen over 40 min. To this solution was added  $\text{Pd}(\text{PPh}_3)_4$  (61 mg, 0.053 mmol) in one portion and the resulting solution was heated at reflux for 24 h under nitrogen. The mixture

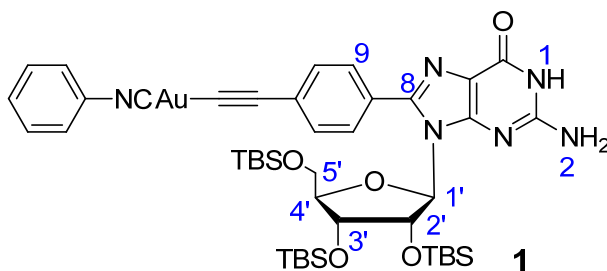
was then cooled to room temperature, concentrated under reduced pressure and then purified by column chromatography on silica gel (gradient eluent 3:1 hexane/ethyl acetate) to afford **4** (292 mg, 71%). <sup>1</sup>H NMR (400 M, CDCl<sub>3</sub>): δ 12.00 (s, 1H); 7.82 (s, 1H); 7.76 (d, *J* = 8.0 Hz, 2H); 7.52 (d, *J* = 8.0 Hz, 2H); 5.89 (d, *J* = 8.0 Hz, 1H); 5.11 (dd, *J* = 4.4, 5.6 Hz, 1H); 4.48 (dd, *J* = 3.2, 4.4 Hz, 1H); 3.99-3.95 (m, 1H); 3.91 (dd, *J* = 7.6, 10.8 Hz, 1H); 3.77 (dd, *J* = 4.0, 10.4 Hz, 1H); 2.58 (hept, *J* = 5.8 Hz, 1H); 1.29 (d, *J* = 1.2 Hz, 3H); 1.27 (d, *J* = 1.2 Hz, 3H); 0.91 (s, 9H); 0.88 (s, 9H); 0.71 (s, 9H); 0.26 (s, 9H); 0.13 (s, 3H); 0.11 (s, 3H); 0.06 (s, 3H); 0.02 (s, 3H); -0.10 (s, 3H); -0.36 (s, 3H). <sup>13</sup>C NMR (100 M, CDCl<sub>3</sub>): 177.8, 155.4, 150.7, 148.8, 146.30, 132.1, 129.7, 129.0, 124.9, 124.4, 104.5, 96.6, 89.1, 84.9, 72.5, 72.0, 62.5, 44.1, 36.9, 26.9, 26.0, 25.9, 25.7, 19.2, 19.0, 18.1, 13.7, -0.0, -4.3, -4.4, -4.5, -5.0, -5.1, -5.2 ppm.

HRMS (FAB) *m/z* calcd for C<sub>43</sub>H<sub>74</sub>N<sub>5</sub>O<sub>6</sub>Si<sub>4</sub> ([M+H]<sup>+</sup>), 868.4716; found, 868.4718.



A mixture of **4** (93 mg, 0.11 mmol) and potassium carbonate (88.8 mg, 0.64 mmol) in tetrahydrofuran-dichloromethane (1:1 v/v, 8 ml) was stirred at room temperature for 18 h. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane and washed with water, followed by dry over anhydrous MgSO<sub>4</sub> and filtration. Removal of the solvent under reduced pressure gave a yellow oil, which was purified by column chromatography on silica gel using dichloromethane-methanol (20:1 v/v) as an eluent to afford **5** (56 mg, yield 72%). <sup>1</sup>H NMR (400 M, CDCl<sub>3</sub>): δ 12.38 (s, 1H); 7.69 (d, *J* = 8.0 Hz, 2H); 7.56 (d, *J* = 8.0 Hz, 2H); 6.61 (br, 2H); 5.78 (d, *J* = 8.0 Hz, 1H); 5.40 (dd, *J* = 4.4, 6.2 Hz, 1H); 4.44-4.47 (m, 1H); 3.90-4.00 (m, 2H); 3.73 (q, *J* = 8.7 Hz, 1H); 3.17 (s, 1H); 0.88 (s, 9H); 0.86 (s, 9H); 0.73 (s, 9H); 0.10 (s, 3H); 0.08 (s, 3H); 0.02 (s, 3H); 0.00 (s, 3H); -0.03 (s, 3H). <sup>13</sup>C NMR (100 M, CDCl<sub>3</sub>): 159.2, 153.3, 152.5, 148.4, 132.3, 132.2, 132.14, 130.0, 129.4, 128.8, 128.7, 128.5, 127.1, 123.6, 117.9, 88.8, 85.1, 83.1, 79.1, 72.4, 71.5, 62.7, 25.9, 25.9, 25.8, 18.4, 18.1, 18.0, -4.3, -4.4, -4.5, -5.0, -5.2, -5.3 ppm.

HRMS (FAB)  $m/z$  calcd for  $C_{36}H_{59}N_5O_5Si_3Na$  ( $[[M+Na]^+$ ]), 748.3722; found, 748.3715.

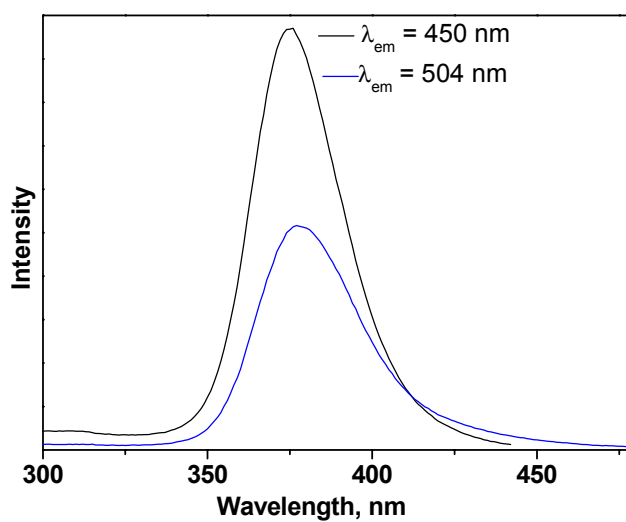


To a tetrahydrofuran-methanol solution (1:9 v/v, 45 ml) of **5** (57 mg, 0.078 mmol) was added Au(tht)Cl (25 mg, 0.078 mmol) and NaOAc (64 mg, 0.78 mmol) at room temperature. The mixture was stirred for 10 h. The yellow precipitate **6** (55 mg, yield 76%) was filtered, washed with water and methanol and dried under vacuum.

To a dichloromethane suspension (1 ml) of **6** (55 mg, 0.060 mmol) was added phenyl isocyanide (6.2 mg, 0.060 mmol) under nitrogen. The mixture was stirred for 1 h at room temperature and became clear. The solvent was removed under reduced pressure. An analytically pure sample **1** (50 mg, yield: 82%) was obtained by column chromatography on silica gel using dichloromethane-methanol (20:1 v/v) as an eluent.

IR (KBr,  $cm^{-1}$ ):  $\nu(N\equiv C)$ , 2209;  $\nu(C\equiv C)$ , 2122;  $^1H$  NMR (400 M,  $CDCl_3$ ):  $\delta$  12.38 (s, 1H, NH); 7.63 (d,  $J = 8.0$  Hz, 2H, H9); 7.50-7.60 (m, 7H, Ar); 6.42 (br, 2H,  $NH_2$ ); 5.84 (d,  $J = 8.0$  Hz, 1H, H1'); 5.41 (dd,  $J = 4, 8$  Hz, 1H, H2'); 4.44 (dd,  $J = 2.8, 4$  Hz, 1H, H3'); 3.96-3.97 (m, 2H, H4' and one of H5'); 3.73 (dd,  $J = 8.0, 12.0$  Hz, 1H, H5'); 0.89 (s, 9H,  $tBu$ ); 0.88 (s, 9H,  $tBu$ ); 0.72 (s, 9H,  $tBu$ ); 0.10 (s, 3H,  $SiCH_3$ ); 0.09 (s, 3H,  $SiCH_3$ ); 0.04 (s, 3H,  $SiCH_3$ ); 0.03 (s, 3H,  $SiCH_3$ ); -0.08 (s, 3H,  $SiCH_3$ ); -0.32 (s, 3H,  $SiCH_3$ ).  $^{13}C$  NMR (100 M,  $CDCl_3$ ): 159.3, 153.0, 152.6, 149.1, 132.6, 131.7, 130.1, 129.1, 127.9, 127.0, 126.1, 124.6 ( $N\equiv CAu$ ), 117.9 ( $C\equiv CAu$ ), 102.9 ( $C\equiv CAu$ ), 88.8 ( $C1'$ ), 85.2 ( $C4'$ ), 72.6 ( $C3'$ ), 71.5 ( $C2'$ ), 62.9 ( $C5'$ ), 26.1, 26.0, 25.8, 18.5, 18.1, 18.0, -4.3, -4.4, -4.5, -5.0, -5.2, -5.3 ppm.

HRMS (FAB)  $m/z$  calcd for  $C_{43}H_{64}AuN_6O_5Si_3$  ( $[[M+H]^+$ ]), 1025.3912; found, 1025.3921.



**Figure S1.** Excitation spectra of **1** (black line: in the absence of KPF<sub>6</sub>, blue line: in the presence of KPF<sub>6</sub> (0.125 eq)).