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ORGANOPALLADIUM COMPLEX CONTAINING 5-AMINO-3*H*-1,3,4-THIADIAZOLIN-2-ONES AS METALLORECEPTOR FOR DNA/RNA NUCLEOBASES

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Abstract- Macrocycles containing two 5-amino-3*H*-1,3,4-thiadiazolin-2-ones linking the 3- and 5-positions of the heterocycle unit and one 1,3-benzenedimethanethiol were prepared *via* the regiospecific *N*-alkylation of 5-amino-3*H*-1,3,4-thiadiazolin-2-one. The 1,3-benzenedimethanethiol sites chelated to palladium metal ion to give an organopalladium metalloreceptor. The structures of the macrocycle and metalloreceptor were established using ^{1}H and ^{13}C NMR, IR, and MS spectrometry. The molecular recognition of the metalloreceptor (**5**) was examined for some DNA/RNA nucleobases using ^{1}H NMR spectrometry. The complexation ability increased in the order uracil/thymine < adenine < cytosine/imidazole.

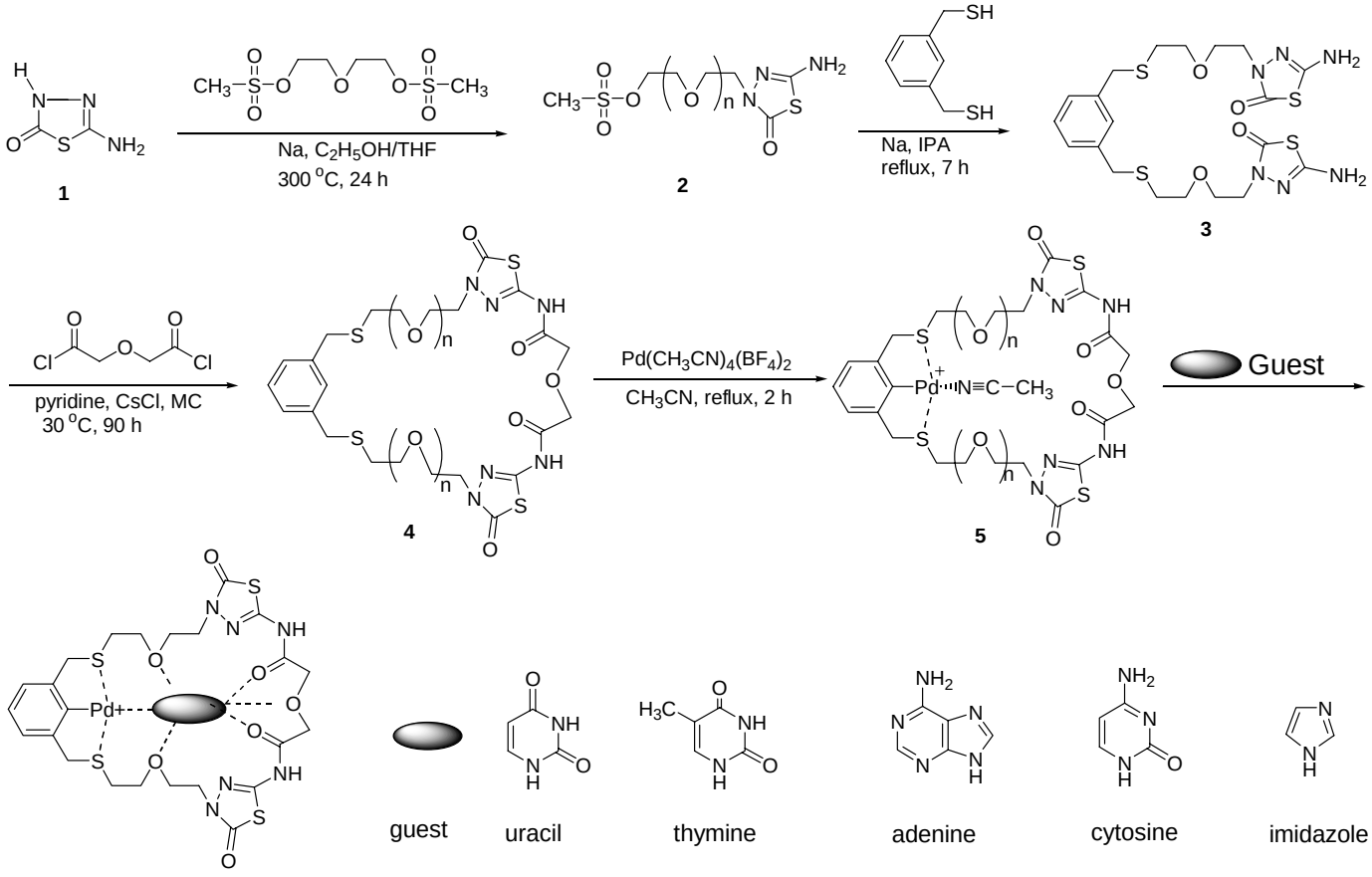
INTRODUCTION

As part of our ongoing study of macrocycles[1-8] containing heterocyclic ring systems, the synthesis of a metalloreceptor composed of two 5-amino-3*H*-1,3,4-thiadiazolin-2-ones and 1,3-benzenedimethanethiol is reported here, along with a study of the molecular recognition of the DNA/RNA nucleobases, cytosine, adenine,

uracil, and thymine, and imidazole. 5-Amino-3*H*-1,3,4-thiadiazolin-2-one is the most stable tautomer form, the lactam form.[9] The NH group of the 5-amino-3*H*-1,3,4-thiadiazolin-2-one at the 3-position is acidic enough to alkylate under basic conditions, and the NH_2 group at the 5-position undergoes acylation.[1] 5-Amino-3*H*-1,3,4-thiadiazolin-2-one provides sites for hydrogen bond formation, and 1,3-benzenedimethanethiol supplies the chelation sites to construct complexes with palladium ions.[10-20]

RESULTS AND DISCUSSION

The tautomeric behavior of 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**1**)[9] and its regiospecific *N*-alkylation[1] under basic conditions were reported. Utilizing these findings, macrocycle containing two 5-amino-3*H*-1,3,4-thiadiazolin-2-ones and 1,3-benzenedimethanethiol subunits was prepared from **1**, as shown in Scheme 1.



Scheme 1. Synthesis of macrocycles and palladium metalloreceptor.

As 1,3-bezenedimethanthiol is a palladation chelation site,[10-20] a 1,3-bezenedimethanthiol moiety was introduced into the macrocyclic compounds for the purpose of chelating palladium. According to the

regiospecific *N*-alkylation of **1**, the reaction of **1** with di(ethyleneglycol) dimethanesulfonate in the presence of $NaOC_2H_5$ in ethanol gave the *N*-alkylated product (**2**). The formation of **2** was confirmed from ^1H and ^{13}C NMR spectra. The NH signal of compound (**1**) was replaced with an NCH_2 at δ 3.92 and 45.8 in the ^1H and ^{13}C NMR spectra, respectively. To introduce 1,3-bezenedimethanthiol, it was *S*-alkylated with **2** under basic conditions ($NaOCH(CH_3)_2$-$(CH_3)_2CHOH$). The formation of **3** was also confirmed from the ^1H and ^{13}C NMR spectra. The SH signal of 1,3-bezenedimethanthiol was replaced by a SCH_2 at δ 2.58 and 30.9 in the ^1H and ^{13}C NMR spectra, respectively. To obtain the target macrocycle containing two 5-amino-3*H*-1,3,4-thiadiazoline-2-thiones and one 1,3-benzenedimethanethiol from **3**, we attempted Cs^+-mediated cyclization,[21, 22] which involves *N*,*N*'-diacylation of **3** at the NH_2 group of the 1,3,4-thiadiazole rings using diglycolyl chloride with a high-dilution technique. Diglycolyl chloride was added to the CH_2Cl_2 solution of **3** over a 72 h period. The structure of the macrocycle was established using ^1H and ^{13}C NMR, IR, and FAB-HRMS spectrum. The successful macrocyclization of **3** to **4** was supported by evidence of *N*-acylation, which indicated that an $NHCOCH_2$ group was replaced the NH_2 functional group at δ 9.58 and 4.20 in the ^1H NMR spectrum and at δ 165.7 and 70.2 in the ^{13}C NMR spectrum. The IR spectrum also shows the carbonyl group of the amide at 1691 cm^{-1}. FAB-HRMS spectrum clearly supported structure (**4**) (643.1137). Moreover, the structure of the macrocycle (**4**) was proven using X-Ray crystallography (Figure 1).

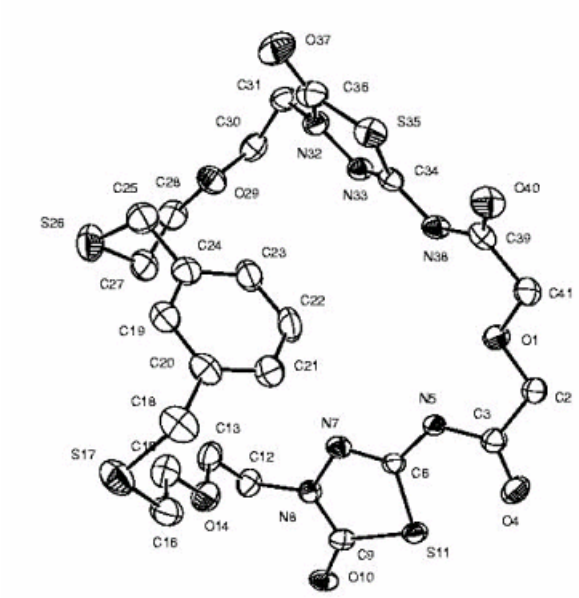


Figure 1. ORTEP drawing of macrocycle (**4**), showing the atomic numbering used for the crystallographic analysis.

The macrocycle (**4**, HL) was easily palladated by refluxing in an acetonitrile solution in the presence of 1 equiv. of $[Pd(CH_3CN)_4][BF_4]_2$. The metalloreceptor was prepared by replacing the labile acetonitrile ligand with 1 equiv. of the substrate molecule. All the spectroscopic and analytical data were consistent with palladation and the formula $[Pd(L)(CH_3CN)][BF_4]$. The resonance of the benzylic CH_2S proton was shifted downfield and was broader in the ^1H NMR spectrum than in that of HL. The effect of palladation was also evident in the ^{13}C NMR spectrum, with the resonance for benzylic carbon atoms shifted downfield by δ 6.8. These results are very similar to those previously reported.[11-21] A strong ion peak for $[Pd(L)]^+$ was observed in the FAB-HRMS spectrum, m/z = 747.0015. The resulting complex is a colorless, air-stable solid that is soluble in most polar organic solvents.

Palladium metalloreceptor (**5)** was used as a host molecule for the molecular recognition study of DNA/RNA nucleobases. Host molecule was dissolved in DMSO-d_6 (0.01 – 0.02 M) and the guest stock solutions in DMSO-d_6 (0.04 – 0.08M) were added several times with small increments until the ^1H NMR chemical shift changes have been stopped. ^1H NMR spectra were recorded at each addition and the chemical shift changes are listed in Table 1.

Table 1. The chemical shift changes of ArCH_2S (4.36 ppm) in metalloreceptor (**5**) upon the addition of guest molecules and calculated complexation constant (K)

Guest	Uracil	Thymine	Adenine	Cytosine	Imidazole
Chemical shift difference of ArCH_2S (Δδ)	0[a]	0[a]	0-0.8[b]	0.4[c]	0.9[c]
Complexation constant, K (M^{-1})	<1[d]	<1[d]	6000	>10000[d]	>10000[d]

[a] No chemical shift changes upon the addition of up to ten equivalents of guest molecules

[b] Chemical shift changes upon the addition of from one to two equivalents of guest molecules

[c] One equivalent of guest molecule was sufficient to notice the chemical shift change.

[d] These values were estimated from the approximation that peaks less than 1/10 of the major peak intensity usually can not be recognized by NMR technique. Thus, K= (0.001 M)/(0.01 M× 0.1 M) = 1 M^{-1} and K=(0.01

M)/(0.001 M× 0.001M)=10000 M^{-1} under the experimental conditions.

Uracil and thymine did not produce any changes in the ^{1}H NMR chemical shift of **5** upon addition of up to ten equivalents, which means there is no interaction between **5** and uracil/thymine. By contrast, significant ^{1}H NMR chemical shifts of **5** were seen with cytosine and imidazole additions. One equivalent of either guest molecule was sufficient to produce the maximum change, so the estimated complexation constants (K) were >> 10^4 (K = [HG]/([H][G]), where, H = host, G = guest, and HG = host-guest complex). Figure 2 shows that the addition of adenine up to two equivalent concentrations resulted in ^{1}H NMR chemical shift changes in **5**. The calculated complexation constant (K) was 6000 M^{-1}. Therefore, the complexation ability of guest molecules to the host molecule (**5)** increased in the order uracil/thymine < adenine < cytosine/imidazole. The possible intermolecular interactions responsible for generating host-guest complexes in our system include hydrogen bonding, σ-donation to Pd, and π-π stacking. An important blank test was performed using macrocycle (**4)**, where σ-donation to Pd is absent. Cytosine, which has the greatest complexation constant with **5**, was added to **4** in DMSO-d_6 solution, no changes were observed in the ^{1}H NMR spectrum. This confirms that the main interaction involved in the molecular recognition of the metalloreceptor (**5)** is σ-donation to the metal rather than hydrogen bonding or π-π stacking. This result is in good agreement with the report that the activation energy for Pd(II)-N bond rupture was obtained as 45 ~ 117 kJ/mol the variable temperature 1-D NMR experiment or 2-D EXSY NMR experiment.[23]

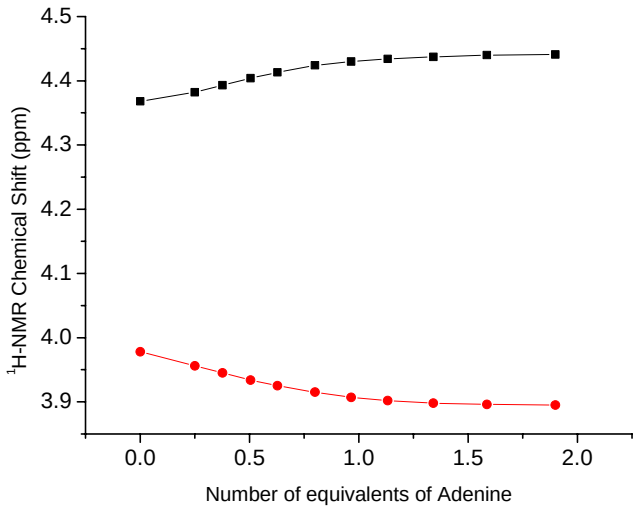


Figure 2. Plot of the ArCH_2S(■) and CH_2N(●) chemical shifts in **5** *vs* number of equivalents of adenine in

DMSO-d_6 solution (concentration of **5** is ranged from 11.3 to 7 mM).

We estimate that the σ-donation to Pd in our system could give that level of the complexation energy whereas hydrogen bonding energy and π-π stacking energy are usually much smaller than 20 kJ/mol. Recently, it was reported that pyrid-2-ylureas bind cytosine in DMF-d_7 with binding constants, K_B, ranging from 30 to 1700 M^{-1}.[24] The ureas have greater binding constants with cytosine than that of our macrocycle (**4)**, but have much smaller constants compared to our organopalladium metalloreceptor (**5**). This is because hydrogen bonding, which plays an important role in urea-cytosine complexation, has a smaller binding energy compared to σ-donation to Pd metal ion.

EXPERIMENTAL

All melting points were determined on an electrically heated Thomas-Hoover capillary melting point apparatus and were uncorrected. The IR spectra were recorded on a Jasco Report-100 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker ARX-400 spectrometer at 400 MHz and 100 MHz respectively with tetramethylsilane as the internal reference. Elemental analyses were carried out on an EA 1110 (CE Instrument). FAB-HRMS spectra were obtained on a JEOL-JMS HX-100/110A spectrometer at Korea Basic Science Institute, Taeduk, Taejon. The molecular recognition study was done using a JEOL JNM-AL400 NMR spectrometer.

The synthesis of 5-amino-3*H*-1,3,4-thiadiazolin-2-one[9] and, di(ethyleneglycol) dimethanesulfonate,[25] and 1,3-benzenedimethanethiol[26] were followed the previous procedures.

5-(5-Amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3-oxapentyl methanesulfonate (2)

5-Amino-3*H*-1,3,4-thiadiazolin-2-one (5 g, 42.7 mmole) was dissolved in C_2H_5OH-Na (1.10 g, 47.9 mmole) solution (100 mL). Di(ethyleneglycol) dimethanesulfonate (11.20 g, 42.7 mmole) in THF (60 mL) was added once to the above solution and the reaction mixture was stirred for 24 h at rt. The end point of reaction was checked by TLC. The salt was filtered off and THF was distilled off under the reduced pressure. The solution was kept in ice box to get rid of remaining di(ethyleneglycol) dimethanesulfonate as precipitate. After removal of di(ethyleneglycol) dimethanesulfonate, C_2H_5OH was also distilled off and chloroform 200 mL was

added and the $CHCl_3$ solution was washed with saturated NaCl solution. The chloroform solution was dried with $MgSO_4$and distilled off all solvent to obtain crude product. This crude product was chromatographed over silica gel using chloroform-methanol (15 : 1) as eluent to give pure product (3.3 g, 27.3%). Oil. R_f: 0.25 ($CHCl_3$: CH_3OH = 15 : 1). IR (NaCl, cm^{-1}): 3327 (NH_2), 1670 (C=O), 1611 (NH). ^1H NMR (400 MHz, $CDCl_3$-d, δ): 4.87 (2H, br, NH_2), 4.35 (2H, t , CH_2OMs, *J*= 4.4 Hz), 3.92 (2H, t, CH_2N, *J*= 5.2 Hz), 3.75 (4H, m , $2CH_2O$), 3.06 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$-d, δ): 167.5 (C=O), 150.8 (C=N), 69.2, 68.4, 68.0 ($3OCH_2$), 45.8 (NCH_2), 37.5 (CH_3). Anal. Calcd for $C_7H_{13}N_3O_5S_2$: C 29.67; H 4.62; S 22.64. Found: C 29.69; H 4.25; S 22.61.

***α,α'-Bis*-[5-(5-amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3-oxapentylthio]-*m*-xylene (3)** To a solution of Na (1.27 g, 55.24 mmol) in 2-propanol (450 mL) 1,3-benzenedimethanethiol (4.5 g, 26.42 mmol) was added and stirred for 1 h at rt. The solution of **2** (14.9 g, 52.59 mmol)-chloroform (40 mL) was added to the above solution and the reaction mixture was stirred at reflux for 7 h. The end point of reaction was checked by TLC. The salt was filtered off and sovent was distilled off under reduced pressure. The residue was dissolved in methylene chloride (500 mL), the CH_2Cl_2 solution was washed with saturated 5% $NaHCO_3$ solution. The methylene chloride solution was dried with $MgSO_4$and all solvent was distilled off to obtain crude product. This crude product was chromatographed over silica gel using *n*-hexane-ethyl acetate-ethanol (5 : 3 : 2) as eluent to give pure product (9 g, 65%). Oil. R_f: 0.51 ($CH_3(CH_2)_4CH_3$: $CH_3CO_2CH_2CH_3$: CH_3CH_2OH = 5 : 3 : 2). IR (cm^{-1}): 3306 (NH_2), 1671 (C=O), 1607 (NH). ^1H NMR (400 MHz, $CDCl_3$-d, δ): 7.27-7.17 (4H, m, C_6H_4), 4.91 (4H, br, $2NH_2$), 3.89 (4H, t, $2CH_2N$, *J*= 4.8 Hz), 3.73-3.69 (8H, m, $2CH_2O$+$2C\underline{H}_2C_6H_4$), 3.59 (4H, t, $2CH_2O$, *J*= 6.4 Hz), 2.58 (4H, t, $2CH_2S$, *J*= 6.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$-d, δ): 167.9 (C=O), 151.2 (C=N), 138.7, 129.8, 128.9, 127.9 (C_6H_4), 71.0, 67.9 ($2OCH_2$), 46.3 (NCH_2), 36.8 ($C_6H_4\underline{C}H_2S$), 30.9 (SCH_2). Anal. Calcd for $C_{20}H_{28}N_6O_4S_4$: C 44.10; H 5.18; S 23.55. Found: C 44.17; H 5.20; S 23.35.

9,13,19,23,36,37-Hexaaza-6,16,26-trioxa-3,11,21,29-tetrathiotetracyclo[29,3,1,$1^{9,12}$,$1^{20,23}$]heptatriaconta-1(35),12(36),20 (37),31(32),33(34)-pentaene-10,14,18,22-tetraone (4)

To a solution of **3a** (3.5 g, 6.4 mmol) in methylene chloride (300 mL), pyridine (1.04 mL, 12.88 mmol) and cesium chloride (1.1 g, 6.5 mmol) were added. Solution of diglycolyl chloride (1.7 g, 9.7 mmole) in methylene

chloride (250 mL) was added for 72 h using syringe pump. After addition of diglycolyl chloride solution, the reaction mixture was stirred for additional 24 h. The end point of reaction was checked by TLC. The salt was filtered off and the solution was washed with saturated NaCl solution and dried with $MgSO_4$. The solvent was distilled off to give product residue. Methylene chloride (5 mL) was added to afford crude precipitate product. The crude product was recrystallized from C_2H_5OH to afford pure product (0.4 g, 10%). mp: 193-194 ^oC. R_f: 0.30 ($CHCl_3$: CH_3OH = 9 : 1). IR (KBr, cm^{-1}) : 3429 (C=ONH), 1691 (C=O), 1642 (C=ONH). ^1H NMR (DMSO-d_6, 400 MHz, δ): 9.58 (2H, br, 2NH), 7.32-7.16 (4H, m, C_6H_4), 4.20 (4H, s, C=OCH_2), 4.03 (4H, t, 2CH_2N, J= 5.2 Hz), 3.76-3.70 (8H, m, 2CH_2O+2C$\underline{H}_2C_6H_4$), 3.60 (4H, t, 2CH_2O, J= 6.4 Hz), 2.58 (4H, t, 2CH_2S, J= 6.4 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 167.5 (C=O), 165.7 ($CH_2\underline{C}$=O), 141.9 (C=N), 138.6, 129.6, 128.7, 127.6 (C_6H_4), 71.2, 68.1 (2OCH_2), 70.2 (C=O$\underline{C}H_2$), 46.7 (NCH_2), 36.5 ($C_6H_4\underline{C}H_2$), 30.8 (SCH_2). FAB-HRMS calcd for $C_{24}H_{31}N_6O_7S_4$ 643.1137, found 643.1134.

X-Ray crystal structure of macrocycle (4)

Macrocycle (**4**) was crystallized from slow evaporation of a solution CH_3CN with tetraethylamonium chloride hydrate. $C_{24}H_{30}N_6O_7S_4$: M.W. 642.78, monoclinic, space group (P2 1/n), a = 15.757(2) Å, b = 10.2769(10) Å, c = 18.2895(17) Å, α= 90°, β= 92.641(9)°, γ = 90°, V = 2958.5(5) $Å^3$, Z = 4, density = 1.443 mg/m^3, μ = 0.374 mm^{-1}, F(000) =1344, T = 293(2) K. The data were collected CAD-4 diffractometer (Enraf-Nonous, 1994) using graphite-mono-chromated Mo-Kα radiation (0.71073 Å). The structure was solved by direct methods (SHELX86) (all non H atoms),[27] followed by full-matrix least-squares refinement (SHELX97)[28] on F^2. Hydrogen atoms were located from ΔF synthesis and positionally refined. All non−hydrogen atoms were anisotropically refined, leading to a final R_1 and wR_2, 0.0660 and 0.1167 respectively, for 5498 unique reflections and 370 refined parameters. S[F^2] 1.013 and $(\Delta/\sigma)_{max}$ was 0.000. Maximum and minimum features in ΔF synthesis are 0.398 and -0.371 e $Å^{-3}$, respectively.

Palladium metalloreceptor (5)

To a solution macrocycle (**4)** (0.5 g, 0.8 mmol) in CH_3CN (120 mL), $[Pd(CH_3CN)_4][BF_4]_2$ (0.3 g, 0.8 mmol) in CH_3CN (15 mL) was added once under a nitrogen atmosphere. The reaction mixture was stirred at rt for 1 h. The color of reaction solution was turned from brown to yellow. Then, it was stirred at reflux for additional 3 h.

The end point of reaction was checked by TLC. The solvent was distilled off to give product residue. The residue was recrystallized from CH_3CN (30 mL) to afford colorless product (0.6 g, 82%). mp: 227-229 ^oC (from CH_3CN). R_f: 0.62 ($CHCl_3$: CH_3OH = 9 : 1). IR (KBr, cm^{-1}): 3222(C=ONH), 1668 (C=O), 1576 (C=ONH). ^1H NMR (DMSO-d_6, 400 MHz, δ): 11.93 (2H, br, 2NH), 6.94-6.80 (3H, m, Ar), 4.36 (4H, s, 2SC$\underline{H}_2$Ar), 4.26 (4H, s, C=OC$\underline{H}_2$), 3.97 (4H, br, 2CH_2N), 3.83 (4H, br, 2CH_2O), 3.75 (4H, br, 2CH_2O), 3.26 (4H, br, 2CH_2S), 2.06 (3H, C$\underline{H}_3$CN). ^{13}C NMR (DMSO-d_6, 100MHz, δ): 168.4 (N-C=O), 166.6 ($CH_2\underline{C}$=O), 152.1 (C_6H_4), 150.1 (C_6H_4), 141.9 (C=N), 124.8 (C_6H_4), 122.6 (C_6H_4), 118.0 ($CH_3\underline{C}N$), 69.6, 67.3 (2OCH_2), 68.6 (C=O$\underline{C}H_2$), 45.9 (NCH_2), 43.7 (S$\underline{C}H_2$Ar), 37.6 (SCH_2), 1.2 ($\underline{C}H_3CN$). FAB-HRMS calcd for $C_{24}H_{29}N_6O_7PdS_4^+$ 747.0023, found 747.0015.

Molecular recognition of 5

The solution of **5 (**7.4 mg, 8.45 X 10^{-6} mol) was prepared in DMSO-d_6 (0.75 mL). The adenine stock solution (2.66 X 10^{-5} mol) was also prepared in DMSO-d_6 (0.75 mL). ^1H NMR spectra of **5** were measured according to the additions of the stock solution. Other nucleobases were studied in similar way. The guest stock solutions were added several times with small increments until the ^1H-NMR chemical shift changes have been stopped.

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