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Highly selective detection of Hg^{2+} ion by push–pull-type purine nucleoside-based fluorescent sensor

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ABSTRACT

Highly selective detection of Hg^{2+} ion has been achieved using the push–pull-type purine nucleoside-based fluorescent sensor **L1**. The sensor **L1** incorporating aza-18-crown-6 at C6 position of purine nucleoside, is highly sensitive and selective toward Hg^{2+} ion in CH_3CN–H_2O mixture (92/8, v/v). The detection limit for the fluorescent sensor **L1** toward Hg^{2+} ion is 7.8×10^{-8}.

1. Introduction

The Hg^{2+} ion has attracted much more concerns for its deleterious effects on human health and natural ecosystem.[1] The toxicity of Hg^{2+} ion, even at very low concentration, can cause several human healthy problems including vision lose, serious cognitive, motion disorders, and prenatal brain injury.[2] In spite of the high toxicity of Hg^{2+} ion, mercury and mercuric salts are still applied extensively in industrial production.[3] Duo to their widely use, the highly sensitive and selective detection analytical method of Hg^{2+} ion is still in great demand.[4] Among numerous sensing methods, fluorescence technology is especially appealing.[5] Up to now, great endeavors have been devoted to develop various outstanding fluorescent sensors.[6] However, most of them were designed based on the thiophilic affinity of the Hg^{2+} ion,[7] and purine nucleosides had never been used as chromophore. Considering the better biological compatibility of purine nucleosides and our systematic work on modification of purine nucleosides,[8] we wish to report a new fluorescent sensor with purine nucleoside as the chromophore and no-sulfur chelator as the receptor for the selective detection of Hg^{2+} ion.

Purine nucleosides are the important subunit of RNA and DNA,[8] however, they are hard to serve as fluorescent sensors due to their weak fluorescent properties.[9] Herein, we designed and synthesized the new purine nucleoside-based fluorescent sensors to enhance their fluorescent properties via push–pull strategy[10]. As shown in Fig. 1, the purine part was used as the chromophore, the electron donating amino derivative was attached to the C6-position of purine to exert a push influence, and the electron-withdrawing aryl group was incorporated to the C8-position of purine to increase the conjugated system and offer a pull effect. By this push–pull effect, the electron flowed across the fluorescent sensor, and its fluorescent properties were improved. In the push–pull-type purine nucleoside-based fluorescent sensor, if a chelating group was introduced into the C6-position of purine, the fluorescent sensor may show high selectivity towards Hg^{2+} ion. Herein, we wish to report

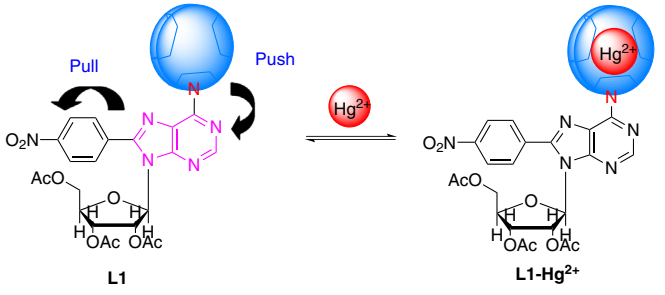

Fig. 1. Push–pull-type purine nucleoside-based fluorescent sensors.

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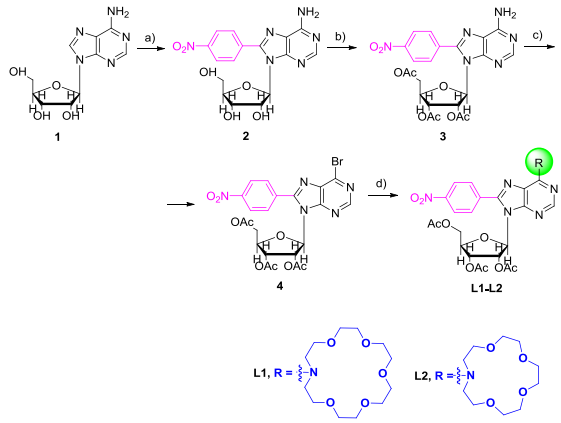
a new push–pull-type purine nucleoside-based fluorescent sensor for the selective detection of Hg^{2+} ion.

2. Results and discussion

Initially, the fluorescent sensors **L1**–**L2** were synthesized as follow: the 4-nitrophenyl group was chosen as the electron-withdrawing group attaching to the C8 position of the adenosine to form a push effect, and the aza-18-crown-6 or aza-15-crown-5 were incorporated to the C6 position of purine nucleosides as chelators (Scheme 1, **L1**–**L2**).



Scheme 1. Synthesis route of **L1**–**L2**. a) 1-Iodo-4-nitrobenzene, $Pd(OAc)_2$, CuI, Cs_2CO_3, N_2; b) Ac_2O, pyridine; c) isoamyl nitrite, $CHBr_3$; d) RH, EtOH, Et_3N.

Subsequently, the fluorescence spectra of **L1**–**L2** (8.0 μM) in the presence of various mental ions (6.0 equiv) were conducted in the solution of CH_3CN–H_2O mixture (92/8, v/v). As shown in Fig. 2A, the addition of 6.0 equiv of Hg^{2+} ion results in an obviously quench fluorescence of **L1** at 403 nm. Meanwhile, a slightly fluorescence quench was observed for Pd^{2+} and Fe^{3+} ions. When Zn^{2+} ions were added, slightly fluorescence enhancements were detected. In addition, other metal ions including Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Pb^{2+} did not result in any noticeable changes. However, when these metal ions were added to fluorescent sensor **L2**, there was no distinctive fluorescence change (Fig. S1). The effect of various metal ions on the fluorescence intensity of **L1** was shown in Fig. 2B, which indicated that the selectivity of **L1** toward Hg^{2+} ion over other metal ions is extremely high.

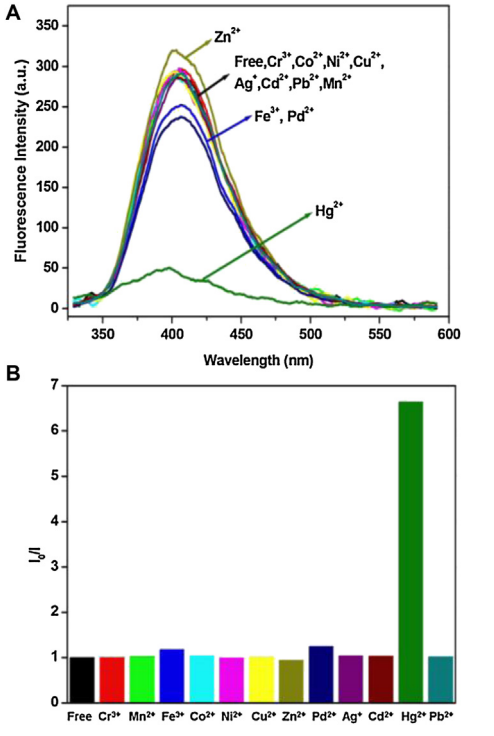


Fig. 2. (A) Fluorescence responses of **L1** (8.0 μM) toward various metal ions (6.0 equiv). (B) Fluorescence responses of **L1** (8.0 μM) upon addition of different metal cations (6.0 equiv), and the bars are relative fluorescence intensities (I_0/I). All the experiments were carried out in CH_3CN–H_2O mixture (92:8, v/v) (λ_{ex}=310 nm).

In order to understand the coordination effect of fluorescent sensor **L1** with Hg^{2+} ion in detail, the fluorescence titration experiments of the sensor **L1** with Hg^{2+} ion were performed in CH_3CN–H_2O mixture (92/8, v/v). As shown in Fig. 3A, when the amount of Hg^{2+} ion was increased from 0 to 30 equiv, the intensities of the fluorescent band of **L1** centered at 403 nm decreased gradually, and the fluorescence was almost quenched completely when 3.0 equiv of Hg^{2+} was added. The change of absorption spectrum of **L1** with different concentrations of Hg^{2+} ion were shown in Fig. S2. Furthermore, the fluorescence intensities of **L1** is linearly proportional to the concentration of Hg^{2+} ions ranging from 0 to 4×10^{-6} mol L^{-1} (Fig. 3B), which indicated that the fluorescent sensor **L1** could be applied for the Hg^{2+}-polluted analysis. The detection limit of the fluorescent sensor **L1** for Hg^{2+} ion is estimated to be 7.8×10^{-8} M.

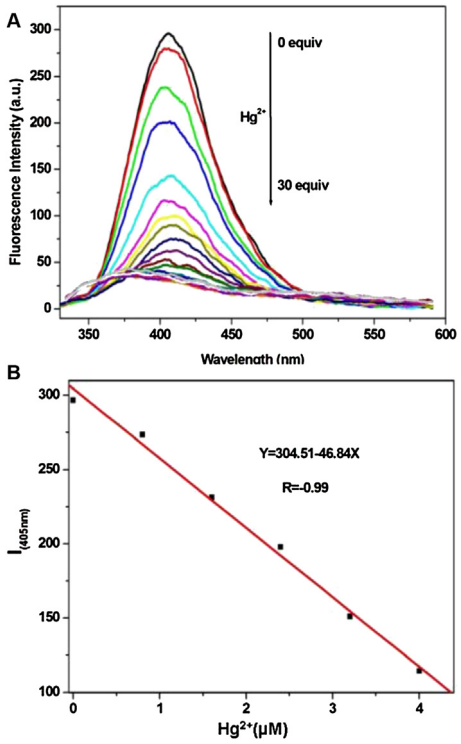


Fig. 3. (A) Fluorescence spectra of **L1** (8.0 μM) in the presence of different concentrations of Hg^{2+} ion (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10, 15, 20, 30 equiv) in CH_3CN–H_2O mixture (92/8, v/v) solution. (B) Plot of fluorescence intensities of **L1** (8.0 μM) in the presence of different concentrations of Hg^{2+} ion (0, 0.1, 0.2, 0.3, 0.4, 0.5 equiv) at 403 nm.

Subsequently, the TPEN titration experiments of **L1**–Hg^{2+} system were tried to testify the coordination between **L1** and Hg^{2+}. When excess amount of TPEN were added, the fluorescence of **L1** recovered gradually (Fig. 4). The fluorescence value of **L1** recovered to the baseline value when the concentrations of TPEN reached to 1.2 equiv of Hg^{2+} ion. It suggested that the binding of Hg^{2+} ion with **L1** was the reason of the fluorescence quenching. To our delight, the

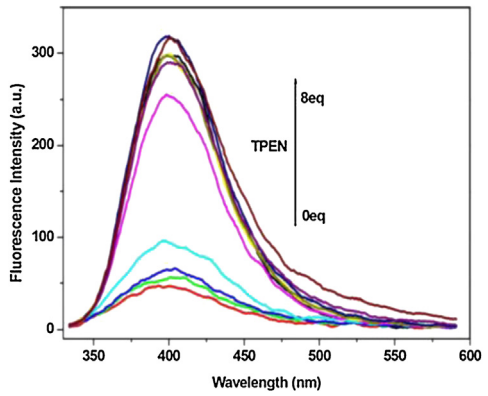


Fig. 4. Fluorescence spectra of the solutions of **L1** (8.0 μM) and Hg^{2+} (32 μM) in the presence of different concentrations of TPEN (0, 0.2, 0.5, 0.8, 1.0, 1.2, 1.5, 2.0, 4.0, 8.0 equiv of Hg^{2+}) in $CH_3CN–H_2O$ mixture (92:8, v/v).

binding process is reversible, which indicated that the sensor **L1** is the first 'On–Off' type purine nucleoside-based fluorescent sensor for Hg^{2+} ion.

In order to examine the potential applicability of **L1** for the selective detection of Hg^{2+} ion, the ions competition experiments were conducted. In $CH_3CN–H_2O$ system (92/8, v/v), various metal ions, including Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Ag^{+}, Cd^{2+}, Pb^{2+} ions were investigated. As shown in Fig. 5A, the sensor **L1** showed almost unchanged responses to Hg^{2+} after adding other competing metal ions. Next, the absorption-based Job plot curve was conducted (Fig. 5B) to investigate the coordination ratio of **L1** with Hg^{2+} ion. The absorption value at 300 nm reached the maximum when X=0.33 [X=[Hg^{2+}]/([Hg^{2+}]+[**L1**])], which indicated that **L1** formed a 2:1 complex with Hg^{2+} ion.

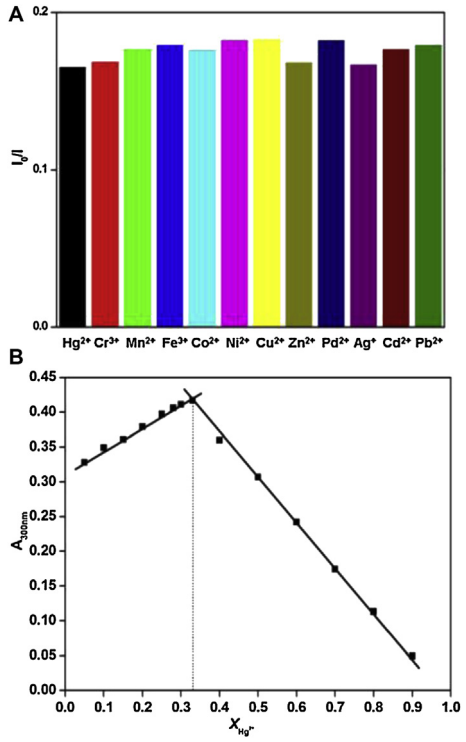


Fig. 5. (A) Fluorescence response of **L1** (8.0 μM) to 48 μM of Hg^{2+} in $CH_3CN–H_2O$ mixture (92/8, v/v) containing 240 μM of various mental ions. (B) The change of the absorption value at 300 nm when the total concentration of Hg^{2+} ions and **L1** is 40 μM and the ratio of Hg^{2+} increased (0.05, 0.1, 0.15, 0.2, 0.25, 0.28, 0.3, 0.33, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9).

Then, the ^1H NMR titration experiments were carried out in CD_3CN to verify the binding mode between **L1** and Hg^{2+} ion. The partial ^1H NMR spectra of **L1** in the presence of different concentration of Hg^{2+} ion were shown in Fig. 6. When the concentration of Hg^{2+} ion increased, an obvious downfield shift of proton Ha at the C2 position of purine nucleoside was observed. Meanwhile, the signals of protons Ha, Hb, and Hc all became broad. These results indicated that there was a coordination effect between Hg^{2+} and the aza-18-crown-6 moiety of sensor **L1**. Based on an overall consideration of various evidences, a proposed binding mode was shown in Fig. 7. The Hg^{2+} ion was fixed by two moleculars of fluorescent sensor **L1**, in which the aza-18-crown-6 moieties were functioned as the binding units.

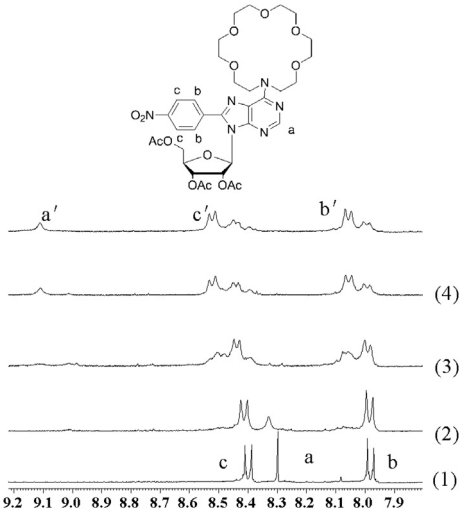


Fig. 6. Partial ^1H NMR (400 MHz) spectra of **L1** in CD_3CN. (1) [Hg^{2+}]/[**L1**]=0; (2) [Hg^{2+}]/[**L1**]=0.2 equiv; (3) [Hg^{2+}]/[**L1**]=0.5 equiv; (4) [Hg^{2+}]/[**L1**]=0.7 equiv; (5) [Hg^{2+}]/[**L1**]=1.0 equiv.

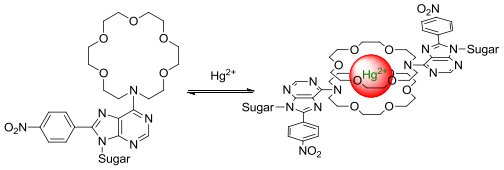


Fig. 7. Proposed interaction model between **L1** and Hg^{2+} ion.

3. Conclusion

A novel push–pull purine nucleoside-based fluorescent sensor **L1**, incorporating aza-18-crown-6 as the binding units, was designed and synthesized. The sensor **L1** displays specific selectivity and sensitivity to Hg^{2+} ion with a low detection limit. Meanwhile, the fluorescent sensor **L1** is linearly proportional to the concentration of Hg^{2+} ions ranging from 0 to 4×10^{-6} mol L^{-1}, which could be applied for the Hg^{2+}-polluted analysis. Further application of the fluorescent sensor **L1** is currently underway.

4. Experimental section

4.1. General information

All reagents and solvents were commercially available and used without further purification. The ^1H NMR spectra were recorded at 400 MHz NMR spectroscopy and ^{13}C NMR spectra were recorded at 100 MHz NMR spectroscopy. Proton chemical shifts δ were given in

parts per million relative to tetramethylsilane ($Si(CH_3)_4$=0.00 ppm) in $CDCl_3$. ^1H NMR coupling constants (*J*) are reported in Hertz (Hz). Multiplicity are indicated as the following: s (singlet), d (doublet), dd (doublet doublet), m (multi). High resolution mass spectra are taken using Q-TOF system, with Electrospray Ionization (ESI) as the ionization method used for the HRMS measurement. Absorption spectra were measured on UV-1700 spectrophotometer. Fluorescence emission spectra were measured FP-6500. All reactions were monitored by thin layer chromatography (TLC). For column chromatography 200–300 mesh silica gel (GF_{254}) was used as the stationary phase.

4.2. Fluorescent response experiments

Stock solutions of **L1**, **L2** in CH_2Cl_2 and each metal salt in H_2O were prepared. Test solutions were prepared by placing 0.1 mL–2.0 mL of the probe's stock solution into test tubes. Then, the CH_2Cl_2 solvent was removed. Subsequently the test samples were dissolved by adding appropriate amount of CH_3CN solution. After that, appropriate amount of each metal stock solution was added. At last, supplement defined amount of H_2O to give the final concentration. After complete mixing, measurements of UV–vis absorption and fluorescent emission were carried out with a 1.0 cm standard quartz cell. For compound **L1**, excitation, 310 nm; emission, 350–500; slit widths for excitation and emission were 5.0 nm. For compound **L2**, excitation, 310 nm; emission, 350–500; slit widths for excitation and emission were 5.0 nm and 10.0 nm.

4.3. General procedure for the synthesis of L1 and L2

*4.3.1. (2R,3R,4S,5R)-2-(6-Amino-8-(4-nitrophenyl)-9H-purin-9-yl)-5-(hydroxymethyl)tetrahydrofuran-3,4-diol (**2**).* To a Schlenk tube containing a stirbar, a mixture of adenosine (0.1335 g, 0.5 mmol), 4-iodonitrobenzene (0.2489 g, 1.0 mmol), $Pd(OAc)_2$ (0.0112 g, 0.05 mmol), CuI (0.2857 g, 1.5 mmol), Cs_2CO_3 (0.4073 g, 1.25 mmol) were dissolved in DMF (3.0 mL). Then the Schlenk tube was fitted with a rubber cap, evacuated and back-filled with nitrogen (this sequence was repeated for three times). The reaction mixture was stirred at 120 °C for 24 h. After completion of the reaction, the DMF was evaporated and the residue was purified by chromatography over silica gel eluting with CH_2Cl_2:MeOH, affording compound **2** with orange solid (33%. yield). ^1H NMR (400 MHz, DMSO-d_6): δ 8.43 (d, *J*=8.4 Hz, 2H), 8.19 (s, 1H), 8.03 (d, *J*=8.4 Hz, 2H), 7.62 (s, br, 2H), 5.82 (d, *J*=8.4 Hz, 1H), 5.75–5.72 (m, 1H), 5.53 (d, *J*=6.4 Hz, 1H), 5.23 (s, 1H), 5.15–5.13 (m, 1H), 4.17 (s, 1H), 3.97 (s, 1H), 3.71 (d, *J*=12.4 Hz, 1H), 3.57 (t, *J*=10.2 Hz, 1H).

*4.3.2. (2R,3R,4R,5R)-2-(Acetoxymethyl)-5-(6-amino-8-(4-nitrophenyl)-9H-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (**3**).* Compound **2** (194.2 mg, 0.5 mmol) and DMAP (6.1 mg, 0.05 mmol, 10 mol %) was dissolved in pyridine and then acetic anhydride (188 μL, 2.0 mmol) was added in drop by drop. The mixture was stirred for 24 h at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by chromatography over silica gel eluting with CH_2Cl_2:MeOH, affording compound **3** with orange solid (51%. yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.42 (d, *J*=9.2 Hz, 2H), 8.00 (d, *J*=8.4 Hz, 2H), 6.49 (dd, *J*=5.8 4.4 Hz, 1H), 6.07 (t, *J*=6.0, 1H), 5.85 (d, *J*=4.0 Hz, 1H), 5.70 (s, br, 2H), 4.57–4.52 (m, 1H), 4.40–4.35 (m, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H).

*4.3.3. (2R,3R,4R,5R)-2-(Acetoxymethyl)-5-(6-bromo-8-(4-nitrophenyl)-9H-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (**4**).* Compound **3** (257.2 mg, 0.5 mmol) was dissolved in tribromomethane, and then isoamyl nitrite (1.35 mL, 10.0 mmol) was dropped slowly. The mixture was stirred for 3.5 h at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by chromatography over silica gel eluting with petroleum: ethyl acetate to give the orange oil compound **4**. The yield of Compound **4** was 55%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.45 (m, 2H), 8.08 (d, 2H), 6.46 (dd, *J*=6.0, 4.0 Hz, 1H), 5.98 (t, 1H), 5.87 (d, *J*=4.0 Hz, 1H), 4.54–4.51 (m, 1H), 4.43–4.40 (m, 1H), 4.37–4.29 (m, 1H), 2.13 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H).

*4.3.4. (2R,3R,4R,5R)-2-(Acetoxymethyl)-5-(8-(4-nitrophenyl)-6-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)-9H-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (**L1**).* To a round-bottom flask compound **4** (0.1154 g, 0.2 mmol) and aza-18-crown-6 (0.0631 g, 0.24 mmol) was dissolved in alcohol. Then, triethylamine (31 μL, 0.22 mmol) was added, after that the reaction mixture was reflux at 80 °C for 8 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue purified by column chromatography on silica gel with petroleum ether:ethyl acetate to give the desired yellow oil product **L1** in 65% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J*=8.8 Hz, 2H), 8.33 (s, 1H), 7.97 (d, *J*=8.8 Hz, 2H), 6.51 (dd, *J*=4.0, 6.0 Hz, 1H), 6.07 (t, *J*=5.8 Hz, 1H), 5.88 (d, *J*=4 Hz, 1H), 4.56–4.52 (m, 1H), 4.40–4.35 (m, 2H), 3.83 (br, 4H), 3.69 (s, 8H), 3.67 (s, 12H), 2.11 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 169.4, 169.4, 148.9, 130.6, 124.1, 120.1, 88.3, 80.2, 80.2, 72.3, 70.9, 70.6, 62.8, 20.8, 20.5, 20.4. HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{34}H_{45}N_6O_{14}$: 761.2988; found: 761.2982.

*4.3.5. (2R,3R,4R,5R)-2-(Acetoxymethyl)-5-(8-(4-nitrophenyl)-6-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)-9H-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (**L2**).* Follow the procedure of compound **L1**, aza-15-crown-5 (0.0631 g, 0.24 mmol) was dissolved in alcohol then triethylamine (31 μL, 0.22 mmol) was added in, after that the reaction mixture was reflux at 80 °C for 8 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue purified by column chromatography on silica gel with petroleum ether:ethyl acetate to give the desired yellow oil product **L2** in 68% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J*=8.8 Hz, 2H), 8.337 (s, 1H), 7.97 (d, *J*=8.8 Hz, 2H), 6.53 (dd, *J*=4.0 6.0 Hz, 1H), 6.06 (t, *J*=5.8 Hz, 1H), 5.88 (d, *J*=4 Hz, 1H), 4.52–4.57 (m, 1H), 4.36–4.39 (m, 1H), 3.88–3.99 (br, 6H), 3.67 (s, 8H), 3.65 (s, 5H), 2.10 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 169.4, 169.35, 154.5, 152.86, 151.9, 148.6, 146.9, 135.8, 130.4, 124.0, 120.4, 88.1, 80.2, 72.2, 71.2, 71.2, 71.1, 70.8, 70.4, 70.4, 70.4, 70.2, 63.0, 20.7, 20.5, 20.4. HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{34}H_{45}N_6NaO_{14}$: 739.2546; found: 739.2551.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.05.050.

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