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PAPER

Bis- and tris-naphthoimidazolium derivatives for the fluorescent recognition of ATP and GTP in 100% aqueous solution†

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Naphthoimidazolium groups can form unique ionic hydrogen bonds with anions as imidazolium moieties, and in addition, they are fluorescent, so no further elaborative synthesis is needed to introduce a fluorescent group. In this paper, three naphthoimidazolium derivatives were synthesized and studied for the recognition of nucleotides. Compound **1** composed of a single naphthoimidazolium group and quaternary ammonium group did not show any significant fluorescent changes with various anions and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP. A tripodal compound **3** bearing three naphthoimidazolium groups and three quaternary ammonium groups, respectively, showed large fluorescence enhancements with UTP, CTP and TTP and moderate fluorescence enhancements with ATP and pyrophosphate and a fluorescence quenching effect with GTP. On the other hand, compound **2** bearing two naphthoimidazolium groups and two quaternary ammonium groups displayed a selective fluorescence enhancement with ATP and a selective fluorescence quenching effect with GTP in 100% aqueous solution.

Introduction

The recognition and sensing of nucleotides is an active area of research due to their biological significance.[1] For example, ATP is a universal energy source and an extracellular signaling mediator in many biological processes.[2] GTP acts as an energy source for protein synthesis and plays an important role in RNA synthesis and the citric acid cycle.[3] UTP is known to participate in enzymatic reactions, such as the many glycosylation processes that are catalyzed by glycosyltransferases and to serve as a donor for energy transduction in organisms.[4] Thymidine nucleotides are essential building blocks in DNA replication and cell division.[5] Although several highly sensitive and selective methods are available for their determination, including high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), enzyme-based methods, *etc.*, there are still some problems due to the sophisticated chromatographic instrumentation and laborious procedures. Since sensors based on anion-induced changes in fluorescence are particularly attractive due to their simplicity and use for *in vivo*/*in vitro* imaging, the development of fluorescent chemosensors to sense various anions has attracted significant attention over the past few years.[6] Many fluorescent chemosensors have been designed for these nucleotides,[7] specifically for ATP,[8] GTP,[9] TTP,[10] UTP,[11] *etc.* Among them, our contributions of GTP[9a] and ATP[8a] utilizing imidazolium derivatives are included, in which imidazolium groups[12] can induce ionic hydrogen bonding interactions between the imidazolium $(C–H)^+$ and phosphate groups. Naphthoimidazolium groups can form these unique ionic hydrogen bonds and in addition, they are fluorescent, so no further elaborative synthesis is needed to introduce a fluorescent group.[13]

In this paper, three naphthoimidazolium derivatives were synthesized and studied for the recognition of nucleotides. Compound **1** (Fig. 1) composed of a single naphthoimidazolium group and quaternary ammonium group did not show any significant fluorescent changes with various anions and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP. On the other hand, tripodal compound **3** bearing three naphthoimidazolium groups and three quaternary ammonium groups, respectively, showed large fluorescence enhancements with UTP, CTP and TTP and moderate fluorescence enhancements with ATP and

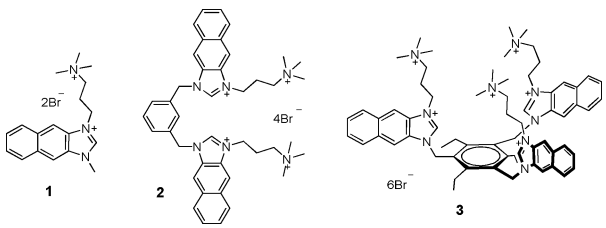

Fig. 1 Structures of compounds **1–3**.

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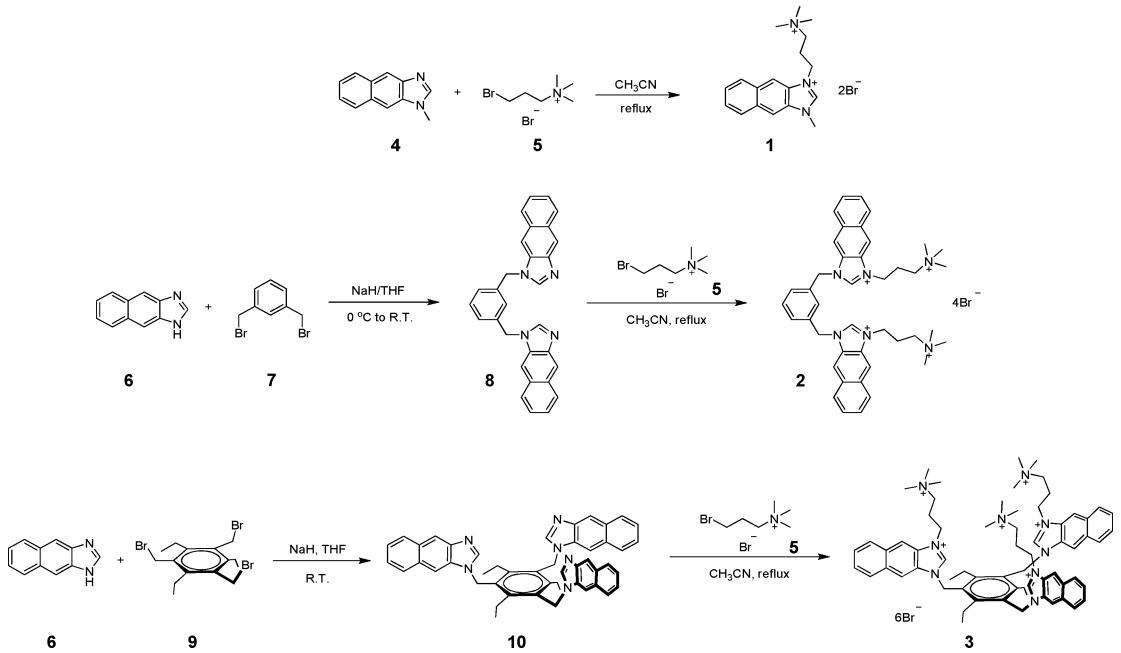

Scheme 1 Synthesis of compounds **1–3**.

pyrophosphate and a fluorescence quenching effect with GTP. Finally, a dipodal system **2** displayed a selective fluorescence enhancement with ATP and a selective fluorescence quenching effect with GTP among the various anions and nucleotides.

Results and discussion

The synthetic routes are explained in Scheme 1. First of all, 1*H*-naphtho[2,3-*d*]imidazole **6**[14] and 1-methyl-1*H*-naphtho[2,3-*d*] imidazole **4**[13b] were synthesized using the published procedures. Then, treatment of **4** with **5** afforded **1** as white solid in a yield of 74%. The intermediate for the ditopic system, **8**, was obtained by the reaction of **7** with NaH and **6** followed by flash chromatography on silica gel ($CHCl_3$: MeOH = 100 : 1) to give **8** as a white solid in a yield of 82%. The ditopic system **2** was synthesized from the reaction of **8** and **5** in a yield of 58%. Finally, **6** was treated with NaH followed by the addition of **9** to give the tripodal intermediate **10**[13a] in a yield of 82% after flash chromatography on silica gel (CH_2Cl_2 : MeOH = 100 : 1), which was reacted again with **5** to afford tripodal system **3** in a yield of 63%. The detailed synthetic procedures and characterization data are given in the Experimental Section and NMR spectra for new compounds can be found in the Supporting Information†.

The fluorescence changes of compounds **1–3** were examined with various anions, such as $CH_3CO_2^-$, $H_2PO_4^-$, CN^-, F^-, Cl^-, I^-, NO_3^-, and pyrophosphate (PPi) and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP at pH 7.4 (20 mM HEPES). As shown in Figure S9†, compound **1** (6 μM) did not display any significant change with these analytes. On the other hand, tripodal compound **3** bearing three naphthoimidazolium groups and three quaternary ammonium groups, respectively, showed large fluorescence enhancements with UTP, CTP and TTP and moderate fluorescence enhancements with ATP and pyrophosphate and a fluorescence quenching effect with GTP (Fig. 2). The fluorescent titrations of **3** with various nucleotides, such as ATP, GTP, UTP, TTP and CTP and pyrophosphate (PPi) were done at pH 7.4 (20 mM HEPES) and the Hill-plots from each fluorescent titration curve were studied and are illustrated in Figure S10–S15†. The association constants for ATP (1.9×10^5 M^{-1}), GTP (6.5×10^4 M^{-1}), UTP (2.1×10^4 M^{-1}), TTP (2.4×10^4 M^{-1}), CTP (2.3×10^4 M^{-1}) and pyrophosphate (PPi) (5.9×10^4 M^{-1}) were also calculated form fluorescent titration (errors <10%).[15] The Hill-plot profiles suggested a 1 : 1 stoichiometry of the host–guest complex between **3** and different guests.[16]

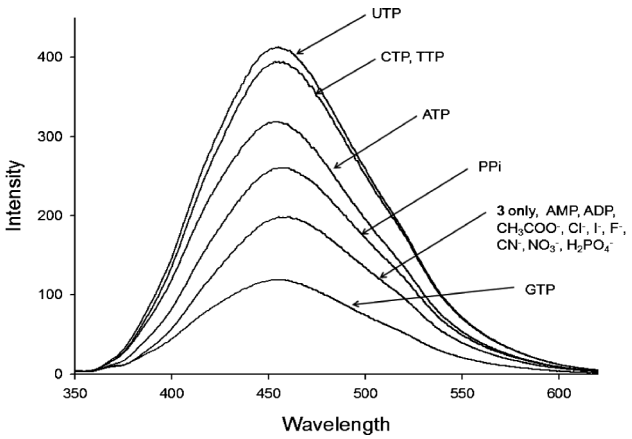

Fig. 2 Fluorescent emission changes of **3** (6 μM) upon addition of $CH_3CO_2^-$, $H_2PO_4^-$, CN^-, F^-, Cl^-, I^-, NO_3^-, and pyrophosphate (PPi) and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP (10 equiv.) at pH 7.4 (20 mM HEPES) (excitation at 326 nm).

The dipodal system **2** was also further studied by fluorescent titrations and NMR experiments. As shown in Fig. 3, about 2-fold fluorescence enhancement was observed for ATP and about 70% of fluorescence quenching was observed in the case of

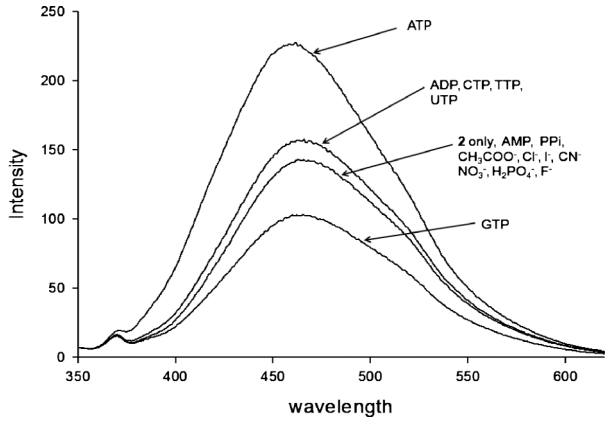

Fig. 3 Fluorescent emission changes of **2** (6 μM) upon addition of $CH_3CO_2^-$, $H_2PO_4^-$, CN^-, F^-, Cl^-, I^-, NO_3^-, and pyrophosphate (PPi) and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP (10 equiv.) at pH 7.4 (20 mM HEPES) (excitation at 326 nm).

GTP. The binding affinity was tighter for ATP. From fluorescent titrations, the association constants for ATP and GTP (Fig. 4) were calculated to be 5.1×10^4 and 2.4×10^4 M^{-1} (errors <10%), respectively.[15] The Hill-plot profiles of the fluorescence titration curve suggested a 1 : 1 stoichiometry between **2** and ATP and GTP (Figure S16†).[16]

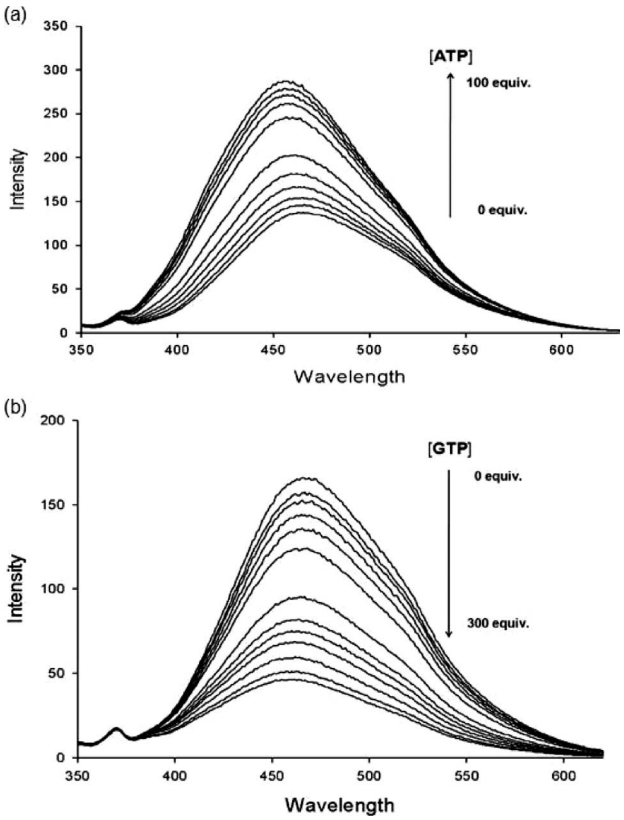

Fig. 4 Fluorescent titrations of **2** (6 μM) upon addition of sodium salt of ATP (a) and GTP (b) at pH 7.4 (20 mM HEPES) (excitation at 326 nm).

The silent responses of **1** with various nucleotides may indicate the weak interaction between one naphthoimidazolium and phosphate anions. The aggregation of imidazoliums can enhance this interaction significantly, which then displayed as a fluorescence increase or decrease of **2** and **3** with different nucleotides. However, we could not observe excimer emissions of naphthoimidazolium moieties for the dipodal and tripodal systems (**2** and **3**), which can be due to positive charge repulsions between naphthoimidazolium and quaternary ammonium arms. Consistent fluorescence quenching effects for compounds **2** and **3** with GTP were also observed in our previous studies[8b,9a] and these quenching effects are due to guanine, which is an efficient quencher, whilst ATP binding usually increases the fluorescence.[8c,9a] Previously, it has been reported by our group that different nucleoside bases can interact with an anthracene derivative with different synergistic effects of π-stacking and electrostatic interactions.[9a] It is also reported that the guanine and adenine moieties can be perpendicular to the anthracene with dipole moments of 6.37 and 1.45 D, respectively.[9a] As explained in our previous study, given the dipole moment of solvent water is ~3 D; molecules solvating the anthracene with larger/smaller dipole moments than the solvent water tend to enhance/reduce the vertical emission transition and thereby to reduce/enhance the fluorescent transition. The fluorescence enhancements of **3** with UTP, CTP and TTP may indicate the different orientation of nucleoside bases in **3**–nucleotide complexes from that in **2**–nucleotide complexes.

To get an insight into the binding pattern of compound **2**, the partial ^{1}H NMR spectra of **2** upon the addition of sodium salt of ATP and GTP in D_2O–DMSO-d_6 (2 : 8, v/v) are presented in Fig. 5 and Fig S18†. A 2D-NOESY NMR spectrum was used to assign the protons in compound **2** in DMSO-d_6 as illustrated in Fig S17†. On the basis of NOESY analyses, the cross peak **A** (Fig S17a†) showed a cross peak between H_h (at 5.91 ppm) and H_b (at 8.77 ppm) and a cross peak **B** (Fig S17b†) illustrated a coupling between H_b and H_d due to their short distance. The proton H_i (at 4.70 ppm) had a cross peak **C** (Fig S17c†) with H_c (at 8.52 ppm), which also showed a cross peak with H_e as shown in the cross peak **D** (Fig S17d†).

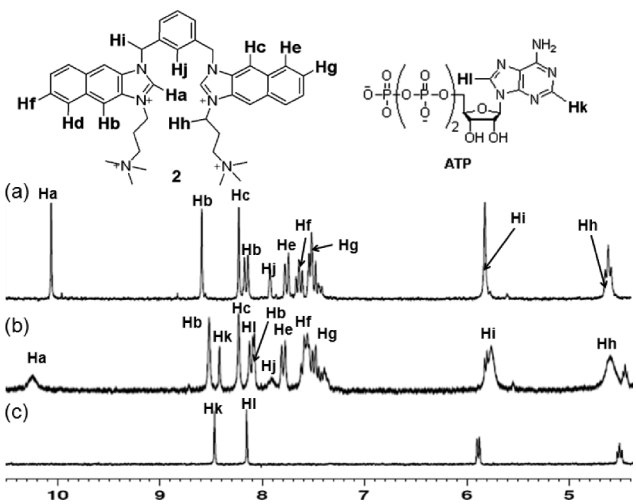

Fig. 5 Partial NMR spectra for (a) host **2** (2 mM), (b) **2**+ATP (1.0 eq.) and (c) ATP at in D_2O–DMSO-d_6 (2 : 8, v/v).

The addition of ATP (Fig. 5, Table 1) and GTP (see Table 1 and Fig. S18†) to a solution of compound **2** in D_2O–DMSO-d_6 (2 : 8, v/v) induced a significant downfield shift of the imidazolium

Table 1 Changes in ^{1}H NMR chemical shifts ($\Delta\delta$) of aromatic protons in **2** with ATP and GTP in D_2O–DMSO-d_6 (2 : 8, v/v)

	H_a	H_b	H_c	H_d	H_e	H_j
ATP	0.187	–0.057	0.018	–0.056	0.048	–0.054
GTP	disappeared	–0.080	0.115	–0.034	0.167	hidden

protons H_a of the naphthoimidazolium moiety of compound **2** and the imidazolium protons disappeared at last due to their deuterium exchange in D_2O. This indicates the strong ionic hydrogen bond interaction between imidazolium and phosphate groups. Interestingly, the phenyl peak H_j showed severe broadness with ATP and GTP due to the phenyl proton's orientation toward ATP and GTP in the complex with them. The H_c and H_e of compound **2** displayed respectively downfield shifts ($\Delta\delta$ = 0.018 and 0.048 ppm), on the other hand, these nucleotides induced upfield shifts of the protons H_b and H_d on the naphthoimidazolium moiety (see Table 1, Fig. 5 and Fig. S18†), which can be attributed to the interaction with adenine base and the anisotropic effect of the *m*-xylyl linker. The H-2 and H-8 of ATP ($\Delta\delta$ = –0.047 and –0.026 ppm respectively), H-8 of GTP ($\Delta\delta$ = –0.0059 ppm), and the anomeric protons showed slight upfield shifts.

To clearly understand the interactions between **2** and ATP/GTP deduced from ^{1}H NMR titration experiments and NOESY analysis, we carried out quantum chemical calculations with the ONIOM method using the complete interacting system retaining expensive MP2 calculations, in a similar manner as done previously for the fluorescent recognition of ATP and GTP.[8b,9a] The optimized structures of 2+ATP/GTP are shown in Fig. 6.

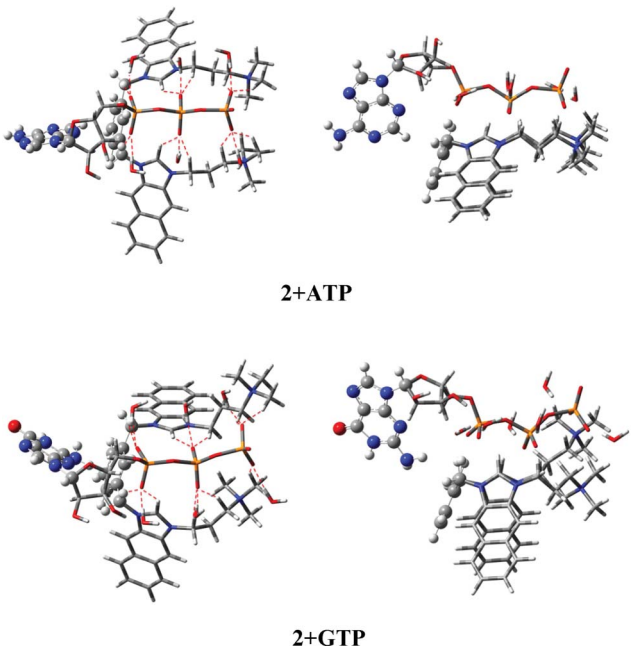

Fig. 6 Top views (left column) and side views (right column) of ONIOM calculation predicted geometric structures of **2** + ATP and **2** + GTP. The red lines show H-bond lengths of less than 1.8 Å.

As shown in Fig. 6, the ball-and-stick type diagrams represent the groups for which high-level (MP2/6-3G*) theory was used in the calculations, while the cylinder type diagrams represent low-level (PM3) theory. Similar to our previous report, we used water molecules to stabilize the negatively charged phosphates. In addition to the electrostatic interactions between phosphates and hydrogen atoms of **2**, the T-shape H–π interaction is operating as seen from the orientation of the phenyl group of **2** in the complex with ATP and GTP. The closest intermolecular C–H (C belongs to phenyl) distances in the H–π interactions for **2** + ATP and **2** + GTP were calculated to be 2.779 and 2.802 Å, respectively. Furthermore, a significant electrostatic interaction was noted to contribute to the interactions from the $(C–H)^+$ of the imidazolium moiety and hydrogen atoms of the alkyl chains. The structural features, such as H–π and electrostatic interactions are very similar to the previous report.

Conclusions

In conclusion, we report herein the synthesis of three naphthoimidazolium derivatives and their recognition of nucleotides *via* fluorescence changes. Compound **1** composed of a single naphthoimidazolium group and quaternary ammonium group did not show any significant fluorescent changes with various anions and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP. On the other hand, tripodal compound **3** showed large fluorescence enhancements with UTP, CTP and TTP and moderate fluorescence enhancements with ATP and pyrophosphate and a fluorescence quenching effect with GTP. Finally, a dipodal system **2** bearing two naphthoimidazolium groups and two quaternary ammonium groups, respectively displayed a selective fluorescence enhancement with ATP and a selective fluorescence quenching effect with GTP among the various anions and nucleotides and their binding modes were further examined *via* NMR study and theoretical calculations. All of these fluorescence experiments were conducted in 100% aqueous solution. These naphthoimidazolium groups can serve not only as the source of ionic hydrogen bonding but also of additional interactions with bases of nucleotides, and finally as a source of fluorescent communications.

Experimental section

Synthesis of 1

100 mg **4**[13b] (0.55 mmol) and 286 mg **5** (1.1 mmol) were added to 30 mL acetonitrile successively. The solution was refluxed for 24 h under N_2. After cooling to room temperature, the precipitate was filtered and washed with cold CH_2Cl_2 to give **1** as white solid (180 mg, 74%). Mp > 250 °C. ^{1}H-NMR (DMSO, 250 MHz) δ 2.57 (m, 2H), 3.14 (s, 9H), 3.62 (m, 2H), 4.23 (s, 3H), 4.73 (t, J = 6.8 Hz, 2H), 7.74 (m, 2H), 8.26 (s, 2H), 8.71 (s, 1H), 8.81 (s, 1H), 10.14 (s, 1H); ^{13}C-NMR(DMSO, 62.5 MHz) δ 22.16, 33.52, 43.80, 52.32, 61.99, 110.88, 110.95, 126.49, 126.53, 128.16, 128.21, 129.91, 130.83, 131.00, 147.06; IR (KBr, cm^{-1}): 3444, 2362, 2335, 1639. HRMS (FAB) calcd for $C_{18}H_{25}BrN_3$ $[M – Br]^+$ 362.1232, found 362.1233.

Synthesis of 8

To a reaction mixture of **6**[14] (500 mg, 3.0 mmol) in THF (40 mL) was added NaH (500 mg, 12.5 mmol, 60% in mineral oil) at 0 °C. After the reaction mixture was stirred for 20 min at 0 °C, **7** (350 mg, 1.3 mmol) was added. After additional stirring for 1 h at room temperature, the reaction mixture was added to 50 ml of water and extracted with CH_2Cl_2. The organic layer was then separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Purification by flash chromatography on silica gel ($CHCl_3$: MeOH = 100 : 1) afforded **8** (476 mg, 82%) as a white solid. Mp: 185 °C. ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 5.19 (s, 4H), 6.97 (m, 3H), 7.15 (s, 1H), 7.29 (m, 4H), 7.42 (s, 2H), 7.62 (s, 2H), 7.89 (d, J = 5.4 Hz, 2H), 7.97 (s, 2H), 8,21 (s, 2H); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 48.51, 105.80, 117.64, 123.75, 124.72, 125.38, 126.85, 127.47, 128.57, 129.91, 130.14, 130.53, 134.20, 136.58, 143.87, 147.08; IR (KBr, cm^{-1}): 3444, 2356, 2340, 1639. HRMS (FAB) calcd for $C_{30}H_{23}N_4$ $[M + H]^+$ 439.1923, found 439.1925.

Synthesis of 2

100 mg **8** (0.23 mmol) and 400 mg **5** (1.5 mmol) were added to 30 mL acetonitrile successively. The solution was refluxed for 24 h under N_2. After cooling to room temperature, the precipitate was filtered and washed with cold CH_2Cl_2 to give **2** as a white solid (127 mg, 58%). Mp > 250 °C. ^{1}H-NMR (DMSO, 250 MHz) δ 2.59 (m, 4H), 3.16 (s, 18H), 3.65 (m, 4H), 4.72 (s, 4H), 5.94 (m, 4H), 7.49–7.67 (m, 7H), 7.95 (s, 2H), 8.22 (m, 3H), 8.54 (s, 2H), 8.79 (s, 2H), 10.53 (s, 2H); ^{13}C-NMR (DMSO, 62.5 MHz) δ 22.10, 44.18, 49.80, 52.39, 62.07, 111.16, 111.29, 126.60, 128.02, 128.18, 128.74, 129.51, 129.77, 130.18, 130.74, 130.79, 134.50, 146.88; IR (KBr, cm^{-1}): 3444, 2362, 2335, 1639. HRMS (FAB) calcd for $C_{42}H_{52}Br_3N_6$ $[M - Br]^+$ 879.1783, found 879.1784.

Synthesis of 3

120 mg **10**[13a] (0.17 mmol) and 400 mg **5** (1.5 mmol) was added to 20 mL acetonitrile successively. The solution was refluxed for 24 h under N_2. After cooling to room temperature, the precipitate was filtered and washed with cold CH_2Cl_2 to give **3** as a white solid (160 mg, 63%). Mp > 250 °C. ^{1}H-NMR (DMSO, 250 MHz) δ 1.19 (m, 9H), 2.60 (m, 6H), 2.81 (m, 6H), 3.17 (s, 27H), 3.70 (m, 6H), 4.88 (s, 6H), 5.87 (m, 6H), 7.75 (m, 6H), 8.27 (m, 6H), 8.92 (s, 3H), 9.04 (s, 3H), 10.37 (s, 3H); ^{13}C-NMR (DMSO, 62.5 MHz) δ 15.68, 22.44, 23.70, 40.44, 44.05, 52.47, 62.00, 111.22, 111.36, 126.81, 128.04, 128.28, 130.29, 130.62, 130.98, 131.17, 145.38, 148.44; IR (KBr, cm^{-1}): 3439, 2354, 2327, 1639. HRMS (FAB) calcd for $C_{66}H_{87}Br_5N_9$ $[M - Br]^+$ 1400.3001, found 1400.3009.

Calculation methods

Optimized structures of **2** + ATP and **2** + GTP complex including water molecules near each oxygen atom of the phosphate groups were performed using ONIOM (MP2/6-31G* calculations for the benzene moiety and nucleic base and PM3 calculations for the remaining parts) by the Gaussian 09 package.[17]

Acknowledgements

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