

## Supporting Information

**A Zn(II) Complex with Large Channels based on 3'-Nitro-Biphenyl-3,5,4'-Tricarboxylic Acid: Synthesis, Crystal Structure, Fluorescent Sensing of ATP, ADP, GTP, and UTP in Aqueous Solution and Drug Delivery**

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## Materials and physical measurements

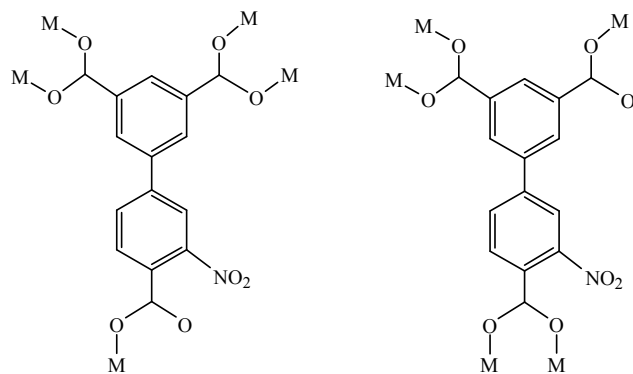
The 3'-Nitro-biphenyl-3,5,4'-tricarboxylic acid reagent, 5-fluorouracil, ibuprofen, sulfadiazine, adenosine triphosphate disodium salt (ATP), adenosine-5'-diphosphate disodium salt (ADP), solvents and others employed were commercially available in the aladdin chemical reagent company and used without further purification. All are analytical reagent grade.

The stock solution of ATP, ADP, various phosphate anions and metal ions were prepared in aqueous solution at pH 7.4 (20 mM HEPES), and kept in the fridge at 0-4 °C. The complex **1** was simply put into the former liquid to form the suspension liquids by ultra sound 30 minutes and to test fluorescence after laying 3 days aside at room temperature.

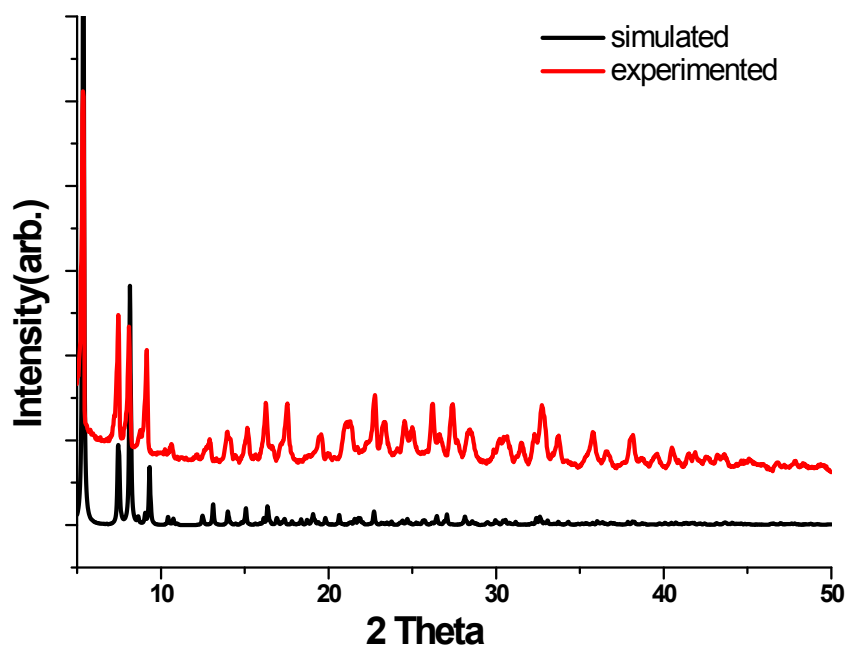
Elemental analyses were performed with an Elementar Vario EL analyzer. Infrared spectra (KBr pellets) were recorded on a Bruker Tensor 37 spectrophotometer in the range 400-4000  $\text{cm}^{-1}$ . Solid state and liquid state fluorescence spectra were recorded on an FL7000 fluorescence spectrophotometer (Japan, Hitachi Company) at room temperature under identical operating conditions. X-ray crystallographic study was based on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation, with data collections at room temperature.<sup>1,2</sup> Semi-empirical absorption correction was applied with the SADABS program.<sup>3</sup> All non-hydrogen atoms were refined anisotropically. The structures were solved by direct methods and refined by full matrix least squares method on F2 using SHELXS 97 and SHELXL 97 programs.<sup>4</sup>

Thermogravimetric analysis (TGA) was used with a HCT-2 thermal analyzer under  $\text{N}_2$  atmosphere, in the temperature range of 25–800 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . UV-vis spectroscopic studies were performed on a 2550 UV-visible spectrophotometer (Shimadzu, Japan). Powder X-ray diffraction (PXRD) data were recorded on a PANalytical X'Pert PRO MPD powder X-ray diffractometer with Cu- $K\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Scanning electron microscope (SEM) images were taken on a Hitachi SU8010 apparatus.

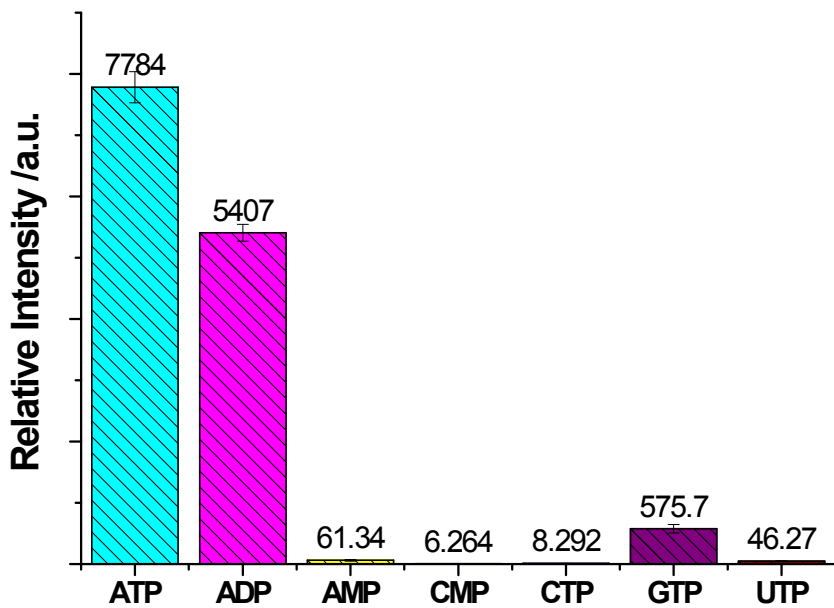
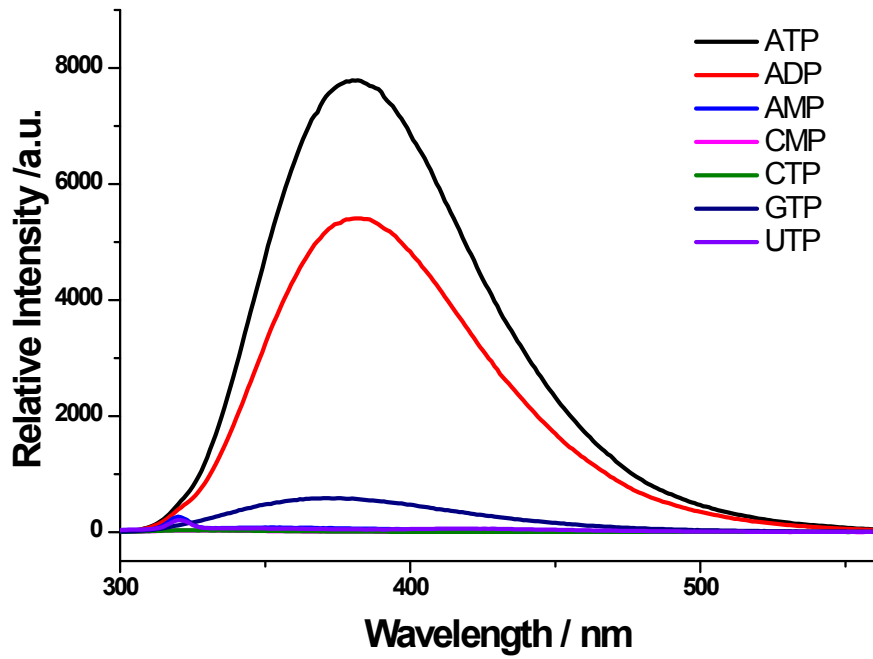
- 1 Stoe, IPDS Manual; X-Red 1.22 Stoe Data Reduction Program; Stoe & Cie GmbH: Germany, 2001.
- 2 Hooft, R. W. W. COLLECT; Nonius BV: Delft, The Netherlands, 1998.
- 3 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1997.
- 4 G. M. Sheldrick. Acta Crystallogr., Sect. A: Found. Crystallogr., A64, 112(2008).



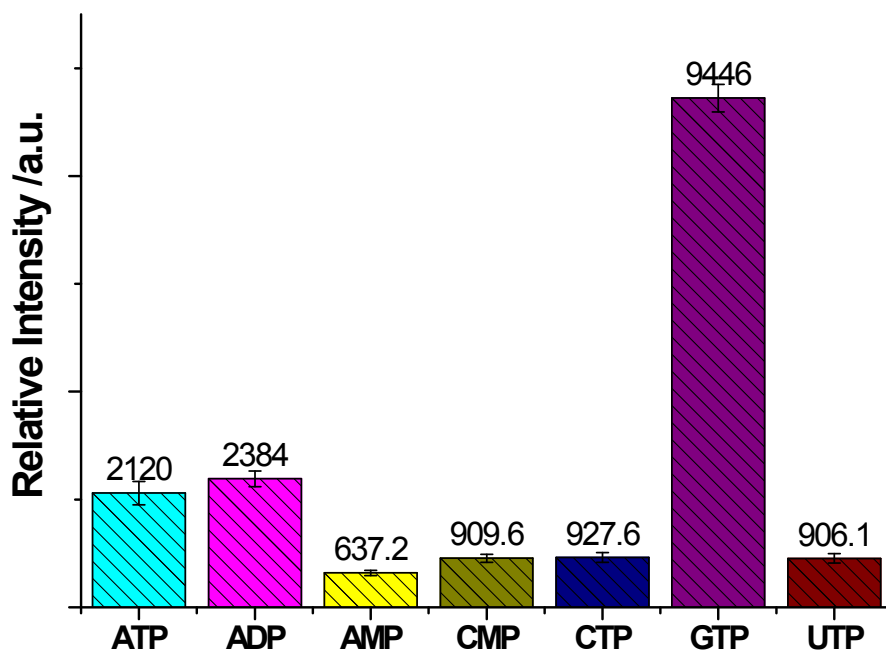
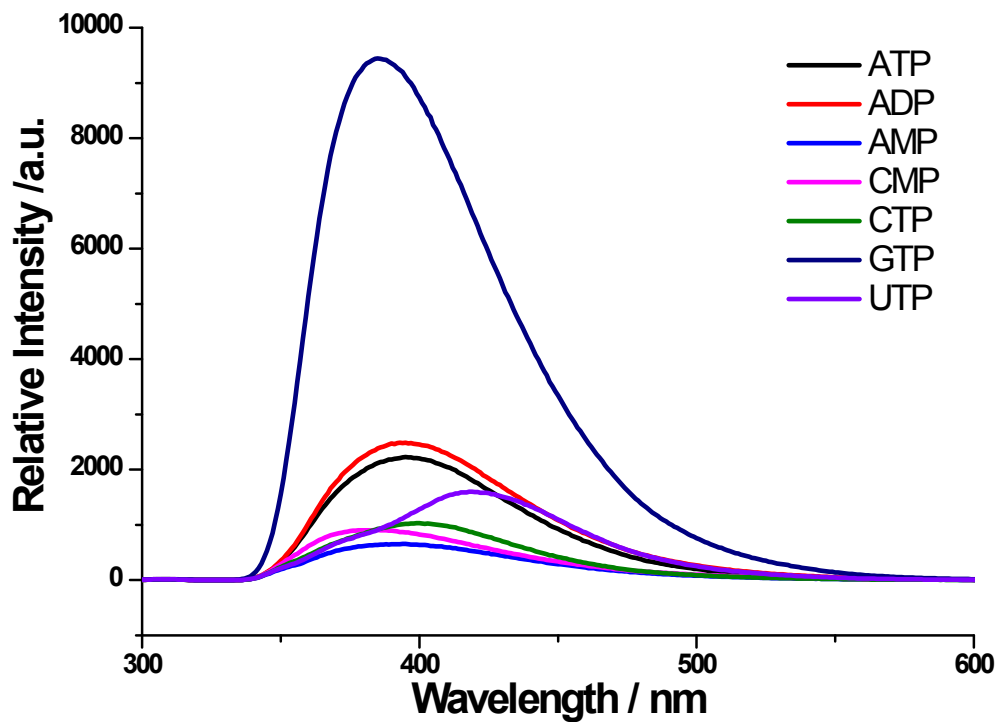
**Scheme S1.** Coordination modes of the HL and L ligand



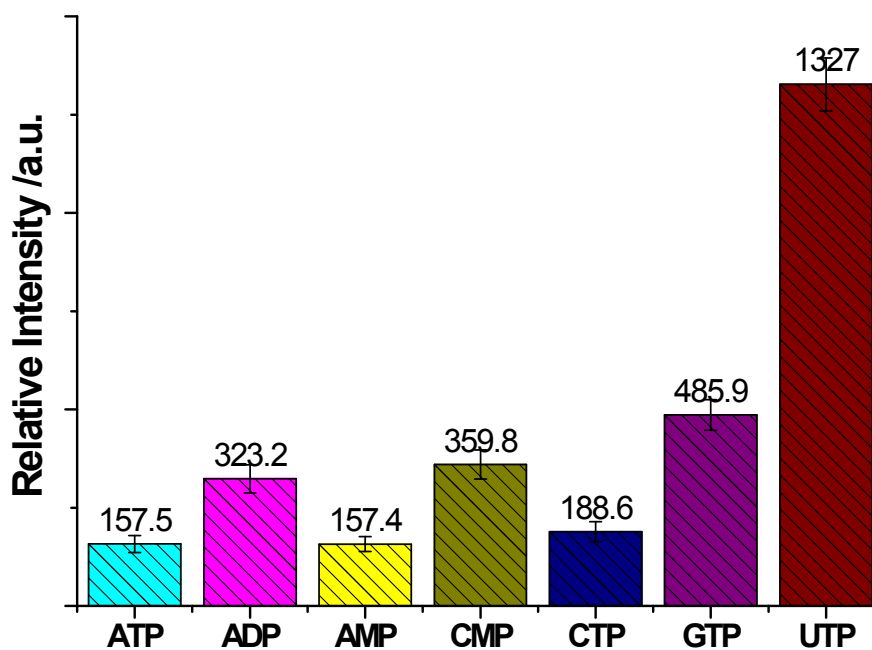
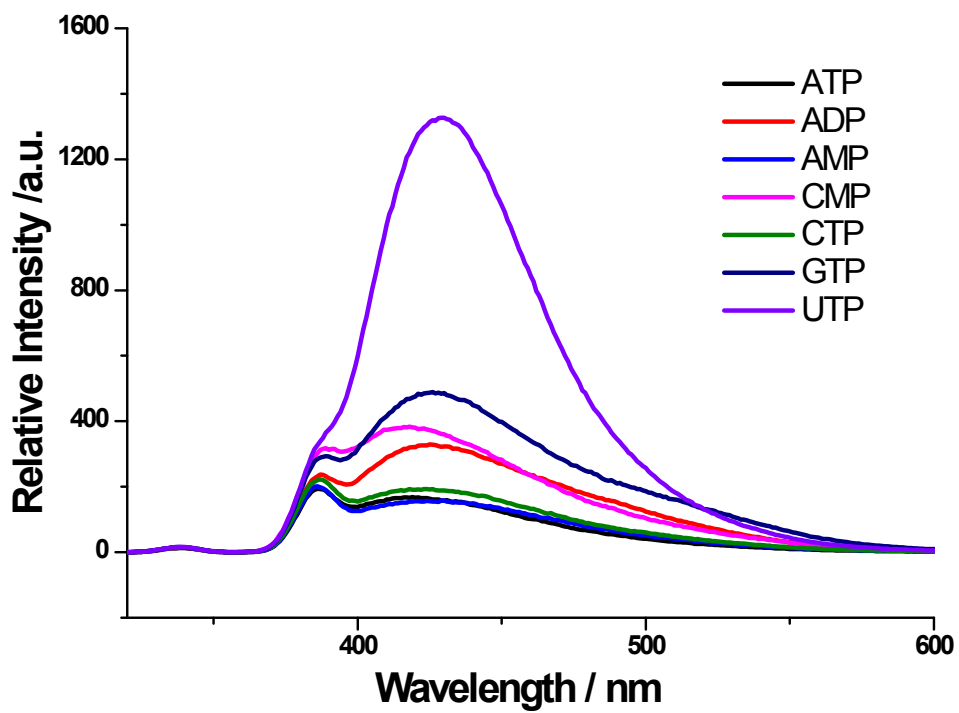
**Figure S1.** Powder X-ray diffraction patterns of complex **1**. PXRD pattern of the as-synthesized sample (red), simulated from single-crystal structure of complex **1** (black).



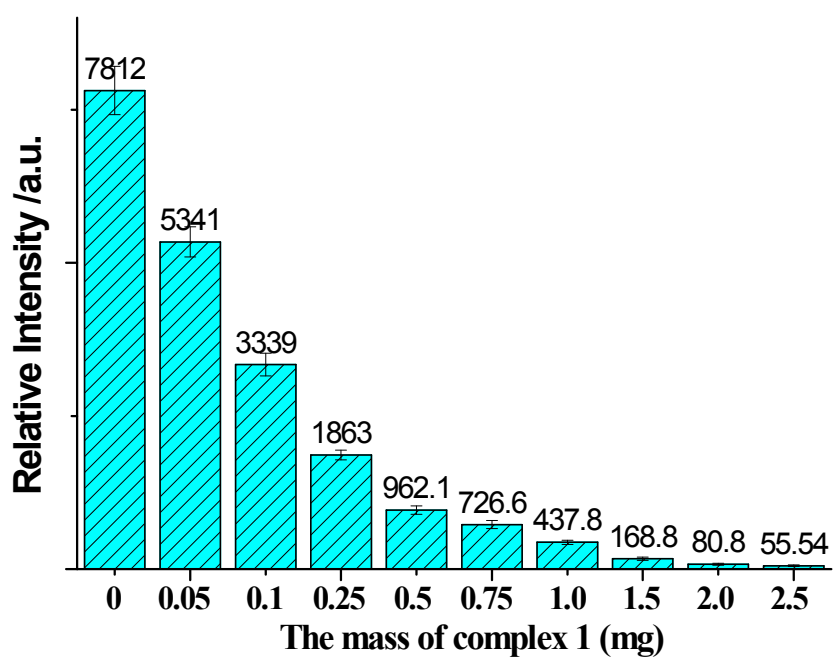
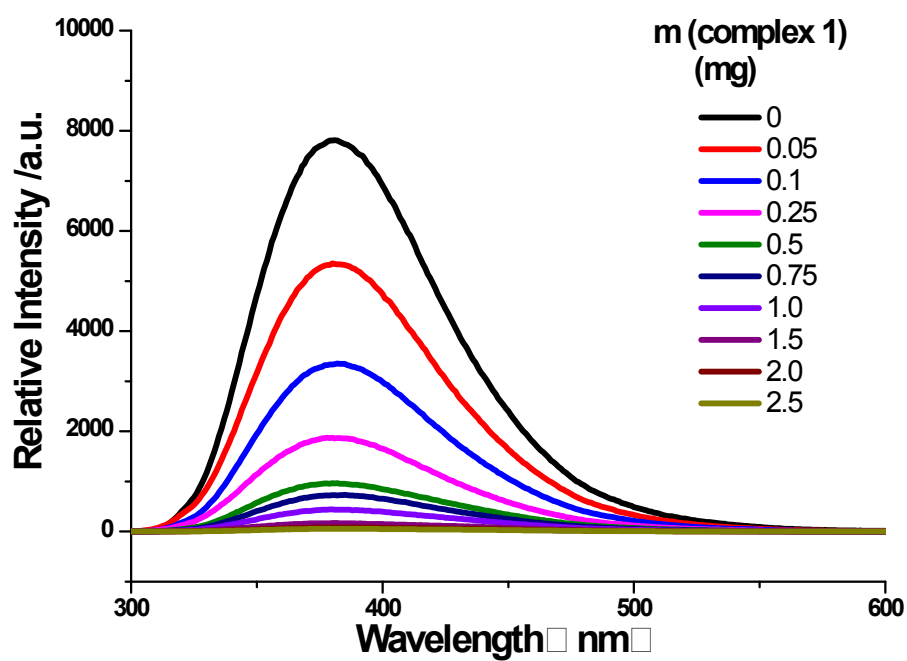
**Figure S2.** Fluorescence emission spectra of many phosphate anions, such as ATP, ADP, AMP, CMP, CTP, GTP, UTP.  $C(\text{phosphate anions})=1 \text{ mM}$  at pH 7.4 (20 mM HEPES),  $T=25 \text{ }^\circ\text{C}$ ,  $\lambda_{\text{EX}}=287 \text{ nm}$ ,  $\lambda_{\text{EM}}=381 \text{ nm}$ ,  $\text{slit}_{(\text{EX})}=5 \text{ nm}$ ,  $\text{slit}_{(\text{EM})}=5 \text{ nm}$ .



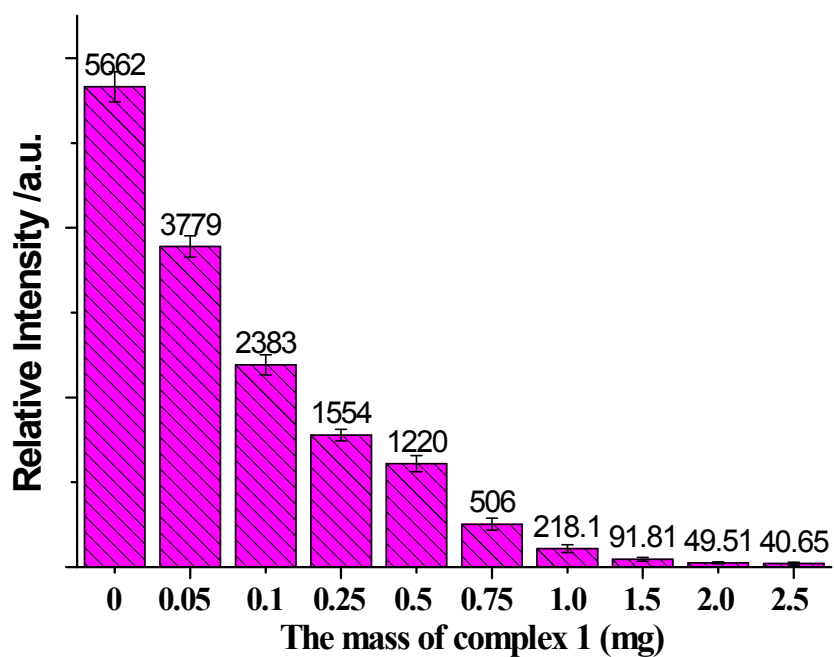
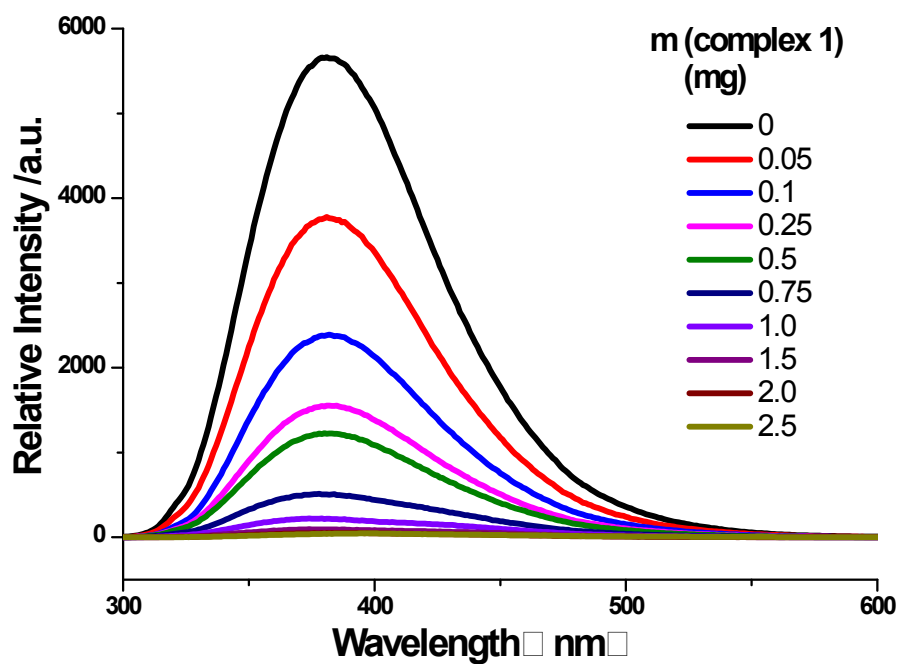
**Figure S3.** Fluorescence emission spectra of many phosphate anions, such as ATP, ADP, AMP, CMP, CTP, GTP, UTP.  $C(\text{phosphate anions})=1 \text{ mM}$  at pH 7.4 (20 mM HEPES),  $T=25 \text{ }^\circ\text{C}$ ,  $\lambda_{\text{EX}}=306 \text{ nm}$ ,  $\lambda_{\text{EM}}=385 \text{ nm}$ ,  $\text{slit}_{(\text{EX})}=10 \text{ nm}$ ,  $\text{slit}_{(\text{EM})}=10 \text{ nm}$ .



**Figure S4.** Fluorescence emission spectra of many phosphate anions, such as ATP, ADP, AMP, CMP, CTP, GTP, UTP.  $C(\text{phosphate anions})=1 \text{ mM}$  at pH 7.4 (20 mM HEPES),  $T=25 \text{ }^\circ\text{C}$ ,  $\lambda_{\text{EX}}=337 \text{ nm}$ ,  $\lambda_{\text{EM}}=430 \text{ nm}$ ,  $\text{slit}_{(\text{EX})}=10 \text{ nm}$ ,  $\text{slit}_{(\text{EM})}=10 \text{ nm}$ .

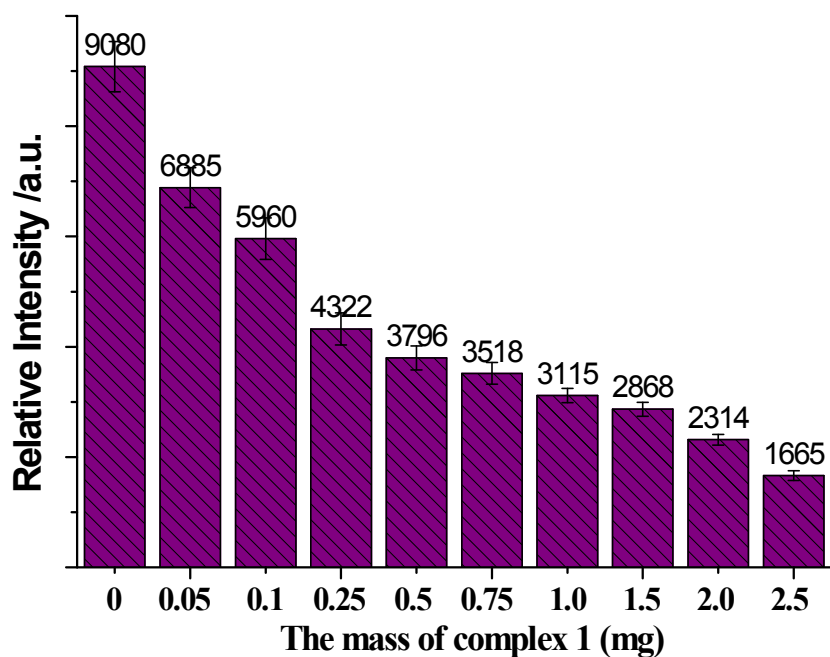
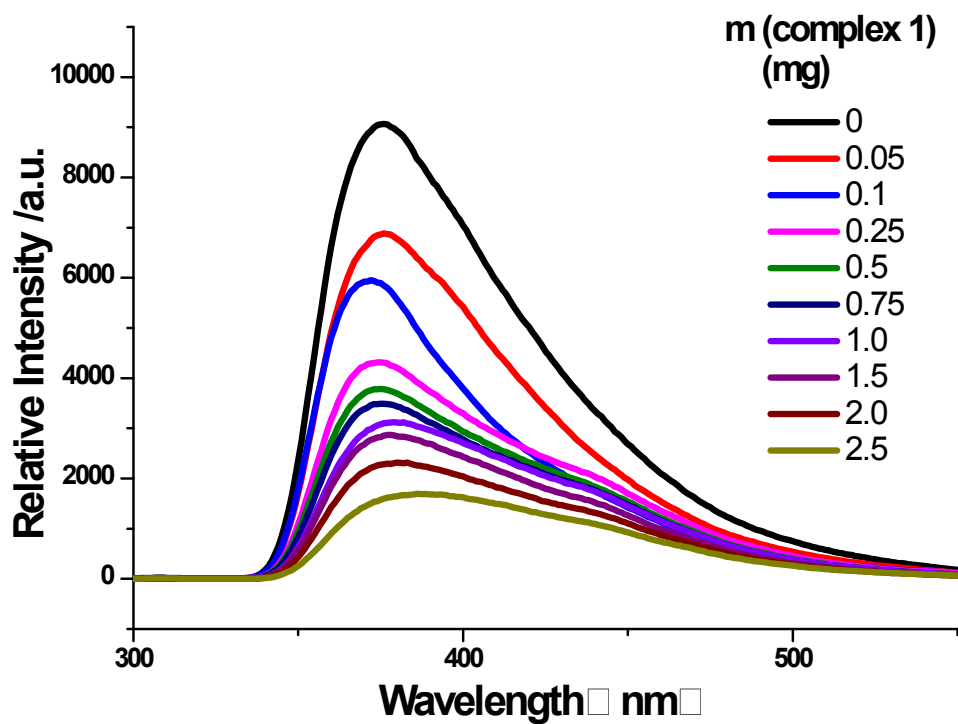


**Figure S5.** Effect of complex 1 on the fluorescence spectra of ATP.  $T=25\text{ }^{\circ}\text{C}$ ,  $C(\text{ATP})=1\text{ mM}$  at pH 7.4 (20 mM HEPES),  $v(\text{ATP})=3\text{ mL}$ , and  $m(\text{complex } 1)=0\text{-}2.5\text{ mg}$ ,  $\lambda_{\text{EX}}=287\text{ nm}$ ,  $\lambda_{\text{EM}}=381\text{ nm}$ ,  $\text{slit}_{(\text{EX})}=5\text{ nm}$ ,  $\text{slit}_{(\text{EM})}=5\text{ nm}$ .

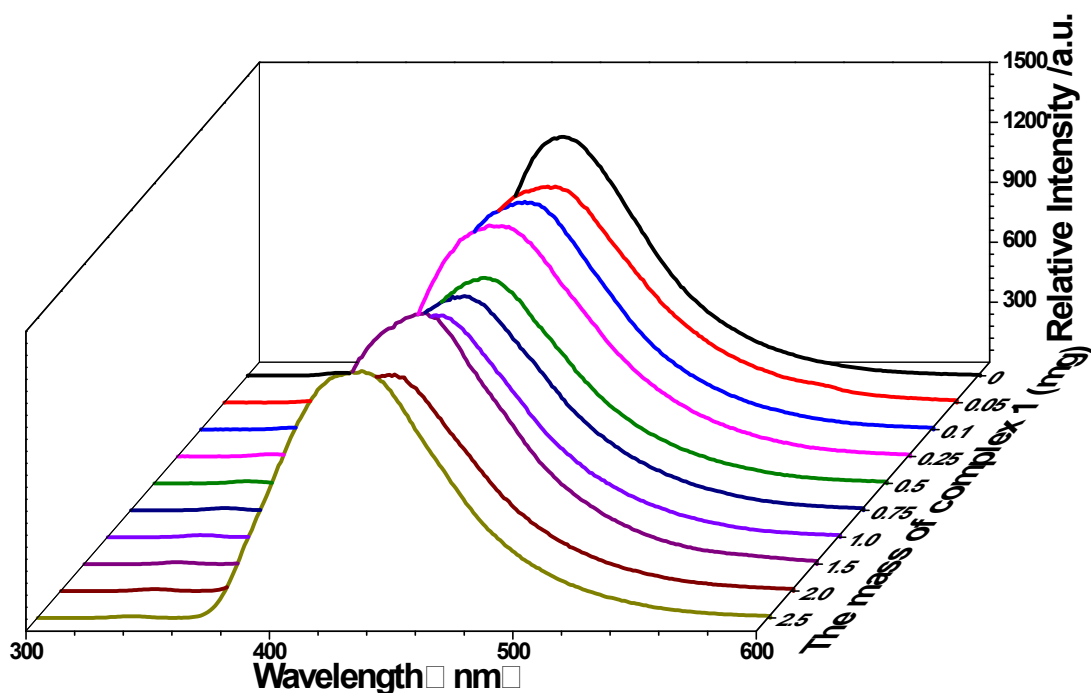


**Figure S6.** Effect of complex 1 on the fluorescence spectra of ADP. T=25 °C, C(ADP)=1 mM at pH 7.4 (20 mM HEPES), v(ADP)=3 mL, and m(complex 1)=0-2.5 mg,  $\lambda_{EX}$ =287 nm,  $\lambda_{EM}$ =381 nm, slit<sub>(EX)</sub>= 5 nm, slit<sub>(EM)</sub>= 5 nm.

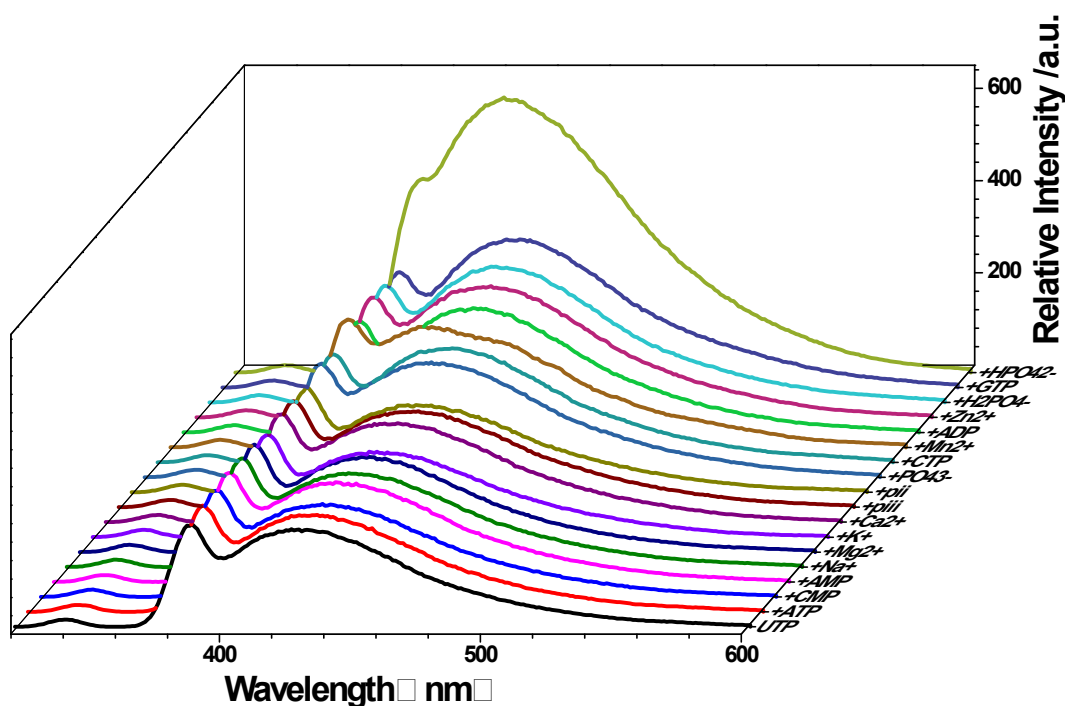




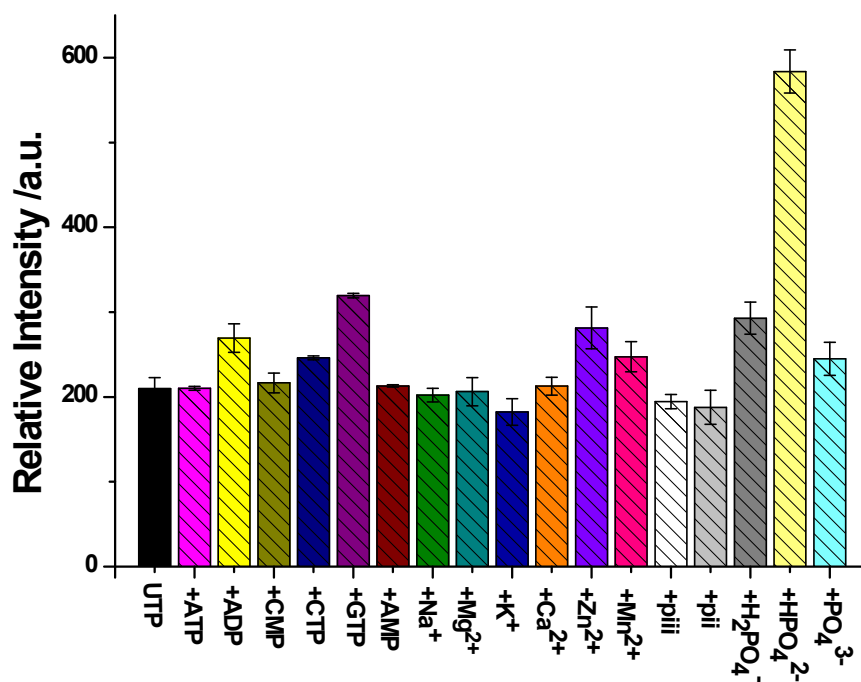
**Figure S7.** Effect of complex 1 on the fluorescence spectra of GTP.  $T=25\text{ }^{\circ}\text{C}$ ,  $C(\text{GTP})=1\text{ mM}$  at pH 7.4 (20 mM HEPES),  $v(\text{GTP})=3\text{ mL}$ , and  $m(\text{complex 1})=0\text{-}2.5\text{ mg}$ ,  $\lambda_{\text{EX}}=306\text{ nm}$ ,  $\lambda_{\text{EM}}=385\text{ nm}$ ,  $\text{slit}_{(\text{EX})}=10\text{ nm}$ ,  $\text{slit}_{(\text{EM})}=10\text{ nm}$ .



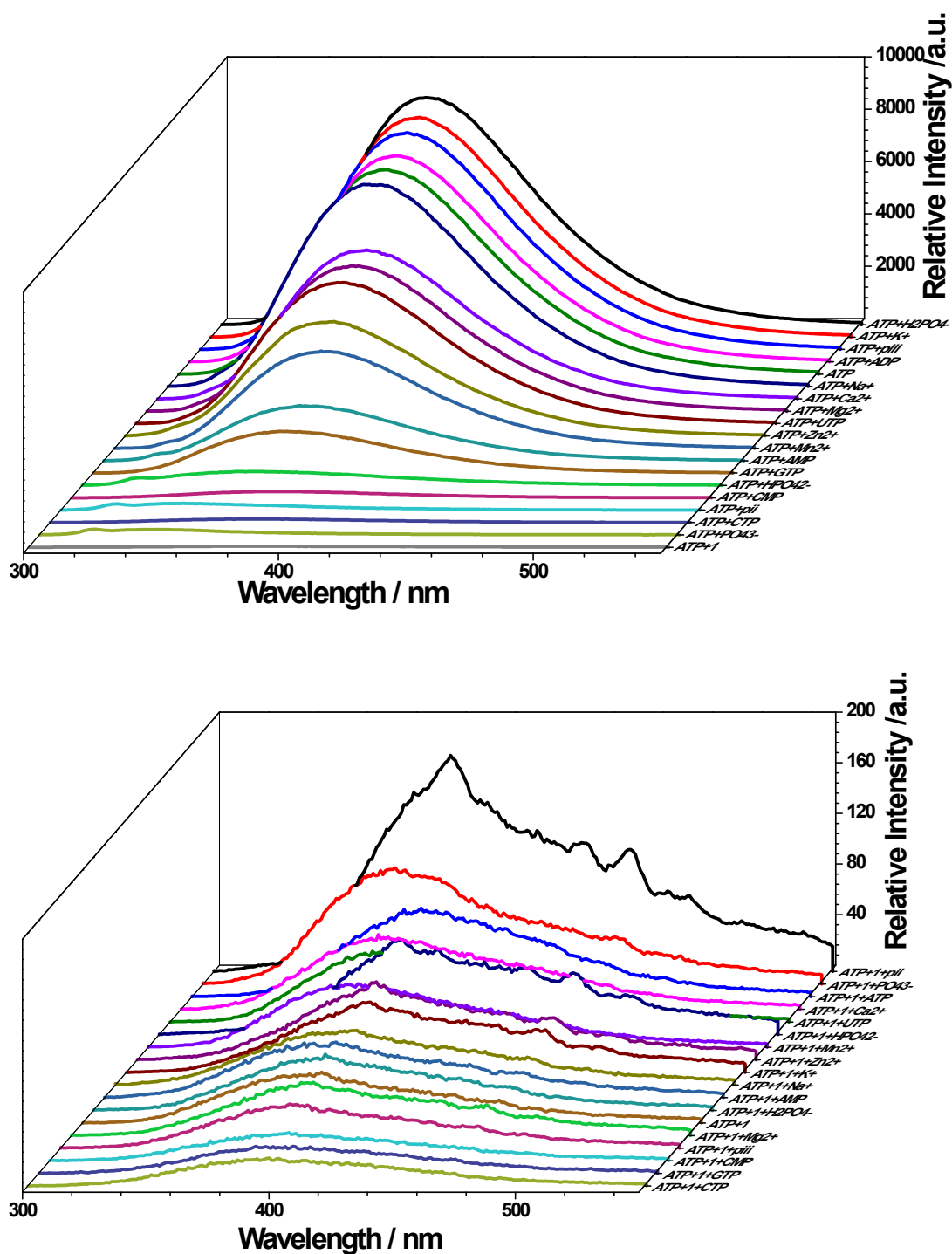
**Figure S8.** Effect of complex **1** on the fluorescence spectra of UTP.  $T=25\text{ }^{\circ}\text{C}$ ,  $C(\text{UTP})=1\text{ mM}$  at pH 7.4 (20 mM HEPES),  $v(\text{UTP})=3\text{ mL}$ , and  $m(\text{complex } 1)=0\text{-}2.5\text{ mg}$ ,  $\lambda_{\text{EX}}=337\text{ nm}$ ,  $\lambda_{\text{EM}}=430\text{ nm}$ ,  $\text{slit}_{(\text{EX})}=10\text{ nm}$ ,  $\text{slit}_{(\text{EM})}=10\text{ nm}$ .



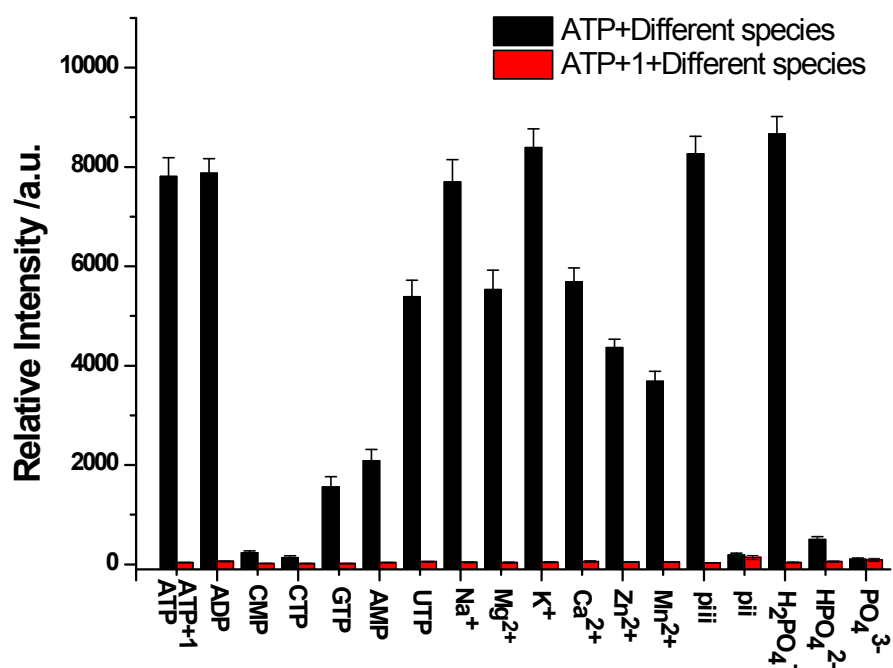
**Figure S9.** Fluorescence emission spectra of UTP and UTP in the presence of different ions and anions, such as ATP, ADP, CMP, CTP, GTP, AMP,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , Piii, Pii,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .  $T=25\text{ }^{\circ}\text{C}$ ,  $\lambda_{\text{EX}}=337\text{ nm}$ ,  $\lambda_{\text{EM}}=430\text{ nm}$ ,  $C(\text{UTP})=0.25\text{ mM}$ ,  $C(\text{different species})=0.25\text{ mM}$  at pH 7.4 (20 mM HEPES),  $V(\text{different species})=3\text{ mL}$ .



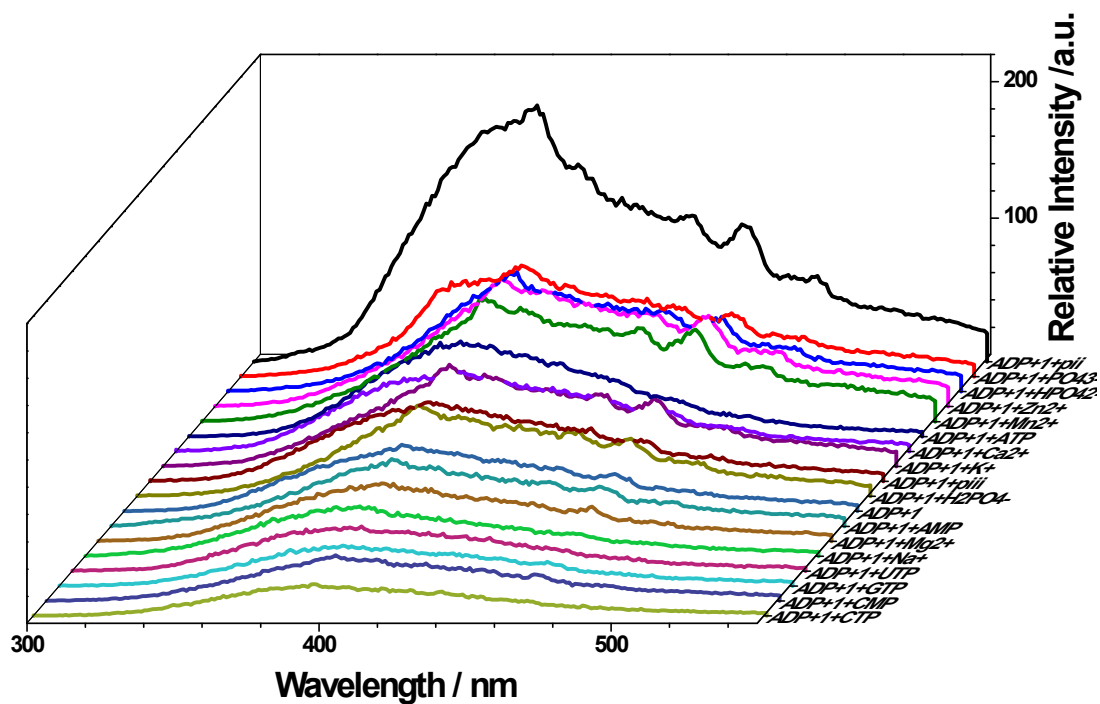
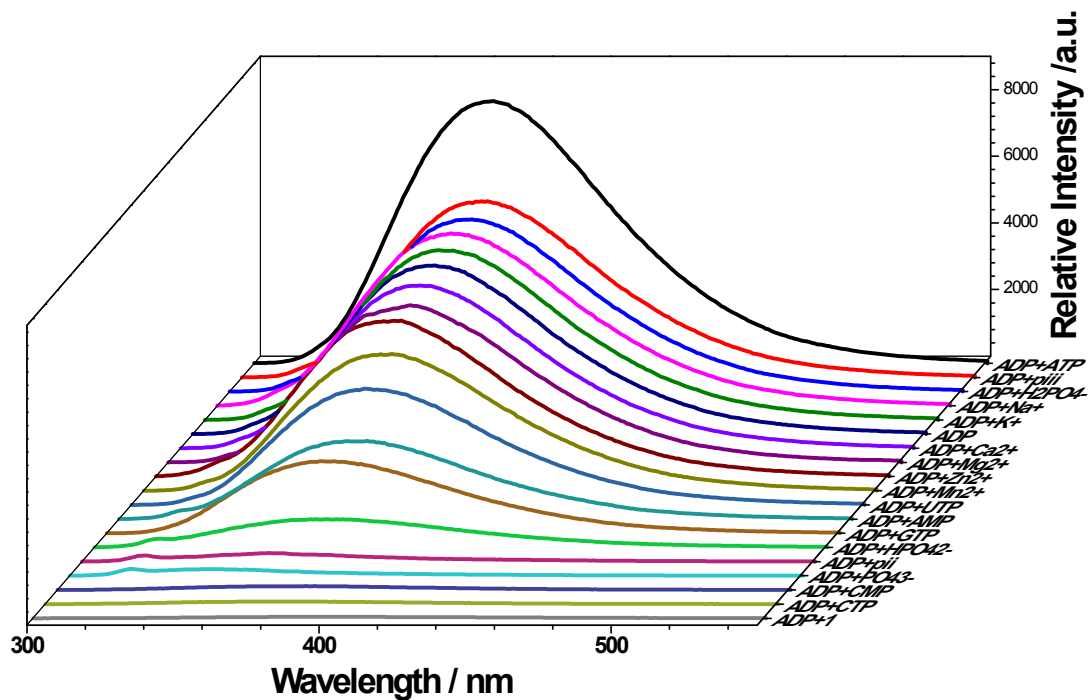
**Figure S10.** Fluorescence responses of UTP (dark bars) and UTP in the presence of different ions and anions (colorful bars), such as ATP, ADP, CMP, CTP, GTP, AMP, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Piii, Pii, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. T=25 °C,  $\lambda_{EX}$ =337 nm,  $\lambda_{EM}$ =430 nm, C(UTP)=0.25 mM, C(different species)=0.25 mM at pH 7.4 (20 mM HEPES), V(different species)=3 mL.



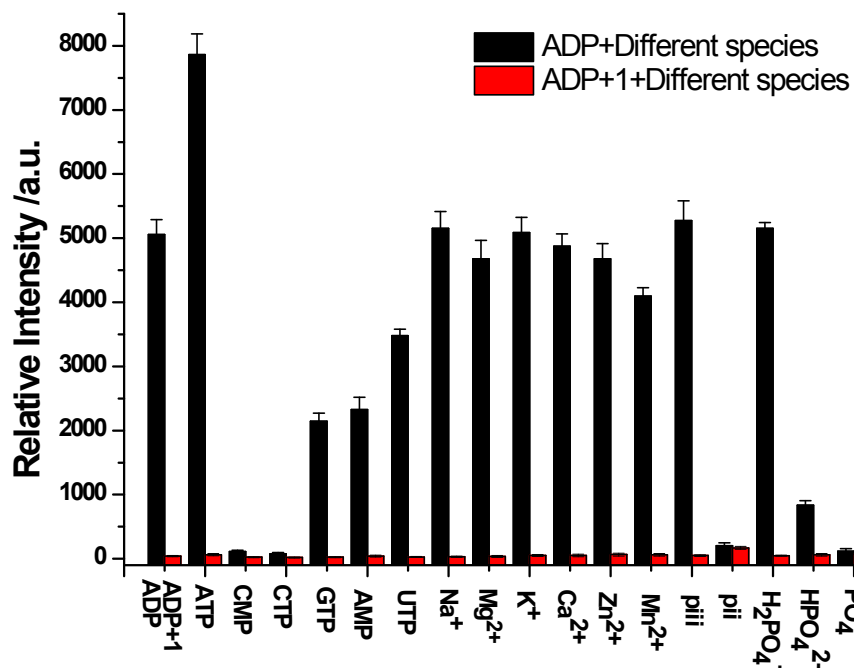
**Figure S11.** Fluorescence emission spectra of ATP and ATP with complex **1** in the presence of different ions and anions, such as ADP, CMP, CTP, GTP, AMP, UTP,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , Piii, Pii,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .  $T=25^\circ\text{C}$ ,  $\lambda_{\text{Ex}}=287\text{ nm}$ ,  $\lambda_{\text{EM}}=381\text{ nm}$ ,  $C(\text{ATP})=1\text{ mM}$ ,  $C(\text{different species})=1\text{ mM}$  at pH 7.4 (20 mM HEPES),  $V(\text{different species})=3\text{ mL}$ , and  $m(\text{complex } \mathbf{1})=2.5\text{ mg}$ ,  $\text{slit}_{(\text{EX})}=5\text{ nm}$ ,  $\text{slit}_{(\text{EM})}=5\text{ nm}$ .



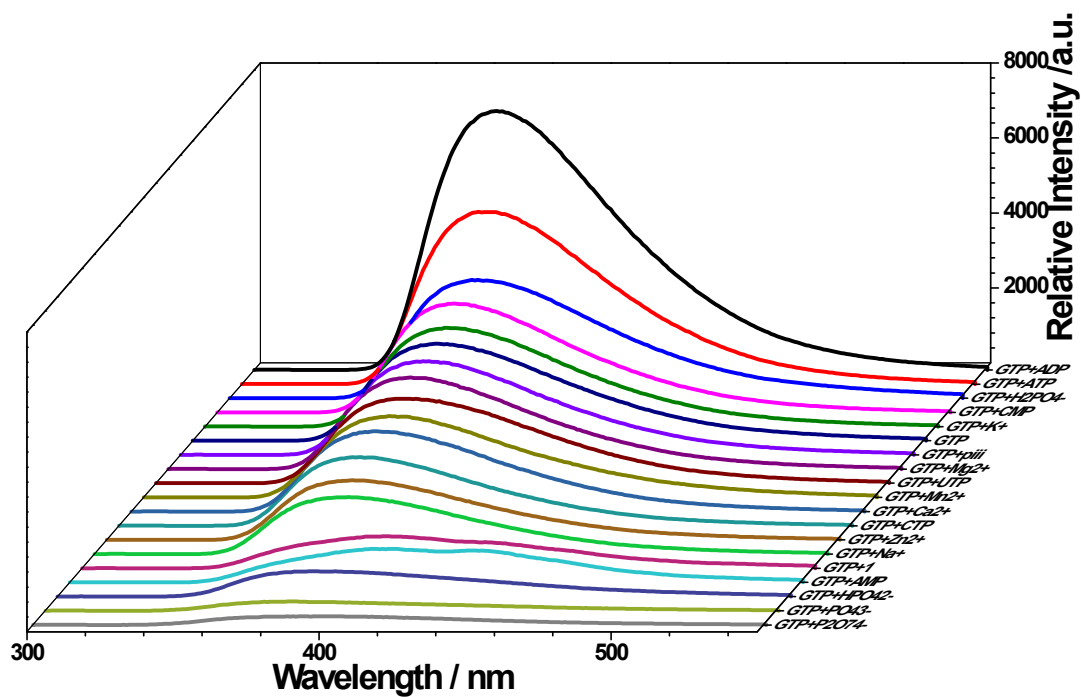
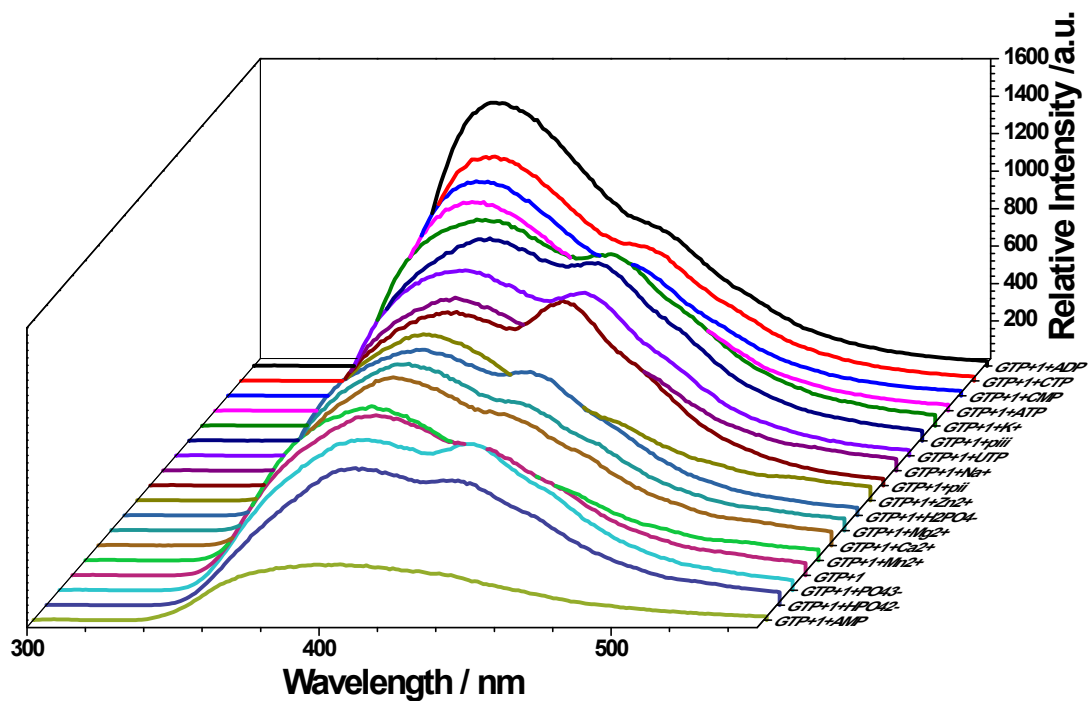
**Figure S12.** Fluorescence responses of ATP (dark bars) and ATP with complex 1 (red bars) in the presence of different ions and anions, such as ADP, CMP, CTP, GTP, AMP, UTP, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Piii, Pii, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. T=25 °C,  $\lambda_{\text{EX}}=287$  nm,  $\lambda_{\text{EM}}=381$  nm, C(ATP)=1 mM, C(different species)=1 mM at pH 7.4 (20 mM HEPES), V(different species)=3 mL, and m(complex 1)=2.5 mg, slit<sub>(EX)</sub>= 5 nm, slit<sub>(EM)</sub>= 5 nm.



**Figure S13.** Fluorescence emission spectra of ADP and ADP with complex **1** in the presence of different ions and anions, such as ATP, CMP, CTP, GTP, AMP, UTP,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , Piii, Pii,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .  $T=25^\circ\text{C}$ ,  $\lambda_{\text{Ex}}=287\text{ nm}$ ,  $\lambda_{\text{EM}}=381\text{ nm}$ ,  $C(\text{ADP})=1\text{ mM}$ ,  $C(\text{different species})=1\text{ mM}$  at pH 7.4 (20 mM HEPES),  $V(\text{different species})=3\text{ mL}$ , and  $m(\text{complex } \mathbf{1})=2.5\text{ mg}$ ,  $\text{slit}_{(\text{EX})}=5\text{ nm}$ ,  $\text{slit}_{(\text{EM})}=5\text{ nm}$ .

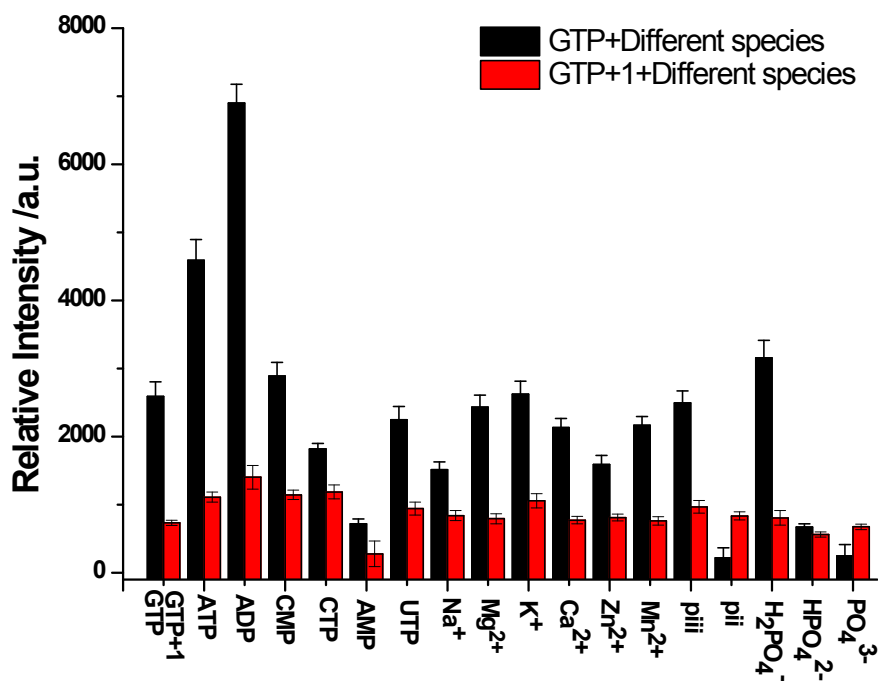


**Figure S14.** Fluorescence responses of ADP (dark bars) and ADP with complex **1** (red bars) in the presence of different ions and anions, such as ATP, CMP, CTP, GTP, AMP, UTP, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Piii, Pii, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. T=25 °C, λ<sub>EX</sub>=287 nm, λ<sub>EM</sub>=381 nm, C(ADP)=1 mM, C(different species)=1 mM at pH 7.4 (20 mM HEPES), V(different species)=3 mL, and m(complex **1**)=2.5 mg, slit<sub>(EX)</sub>= 5 nm, slit<sub>(EM)</sub>= 5 nm.

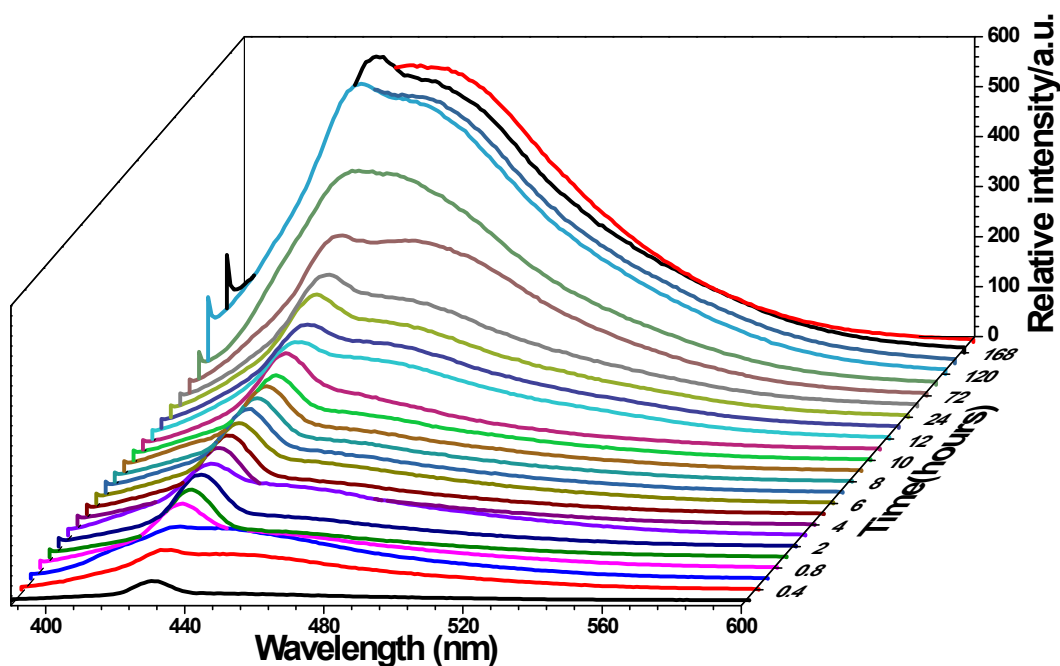


**Figure S15.** Fluorescence emission spectra of GTP and GTP with complex 1 in the presence of different ions and anions, such as ATP, ADP, CMP, CTP, AMP, UTP, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Piii, Pii, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. T=25 °C, λ<sub>EX</sub>=306 nm, λ<sub>EM</sub>=385 nm, C(GTP)=1 mM, C(different species)=1 mM at pH 7.4 (20 mM HEPES), V(different species)=3 mL, and m(complex 1)=2.5 mg, slit<sub>(EX)</sub>= 5 nm, slit<sub>(EM)</sub>= 10 nm.

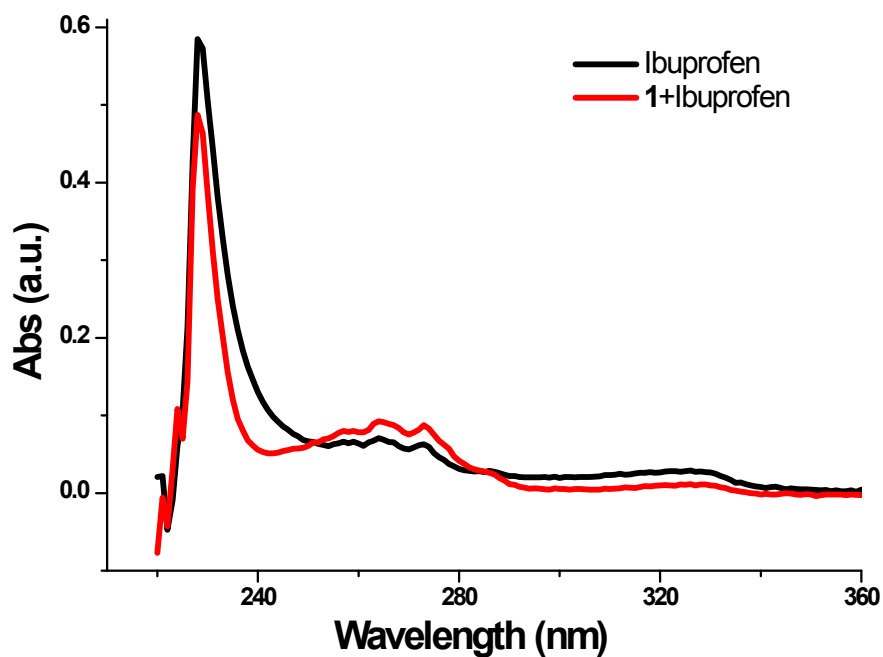




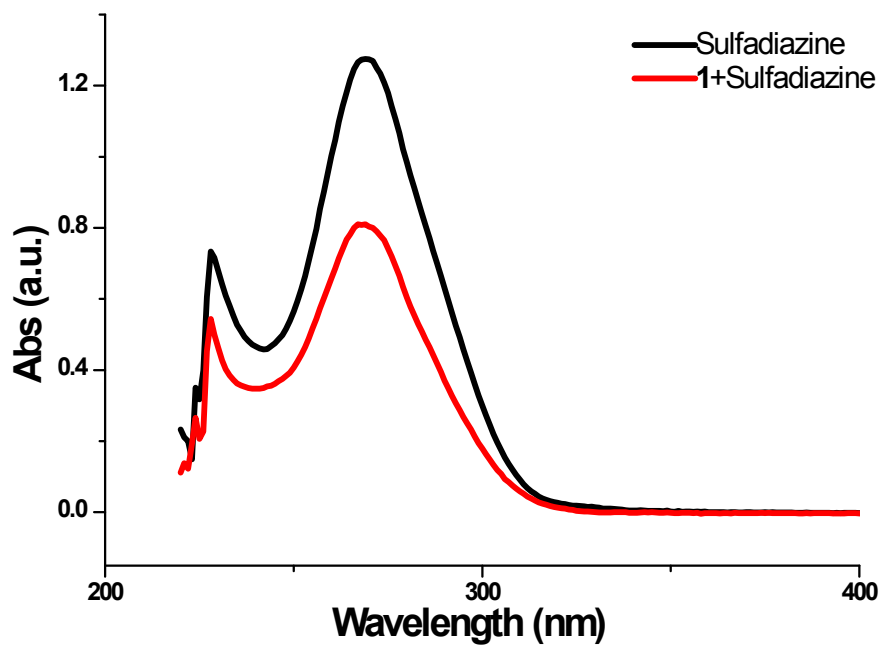
**Figure S16.** Fluorescence responses of GTP (dark bars) and GTP with complex **1** (red bars) in the presence of different ions and anions, such as ATP, ADP, CMP, CTP, AMP, UTP, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Piii, Pii, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. T=25 °C, λ<sub>EX</sub>=306 nm, λ<sub>EM</sub>=385 nm, C(GTP)=1 mM, C(different species)=1 mM at pH 7.4 (20 mM HEPES), V(different species)=3 mL, and m(complex **1**)=2.5 mg, slit<sub>(EX)</sub>= 5 nm, slit<sub>(EM)</sub>= 10 nm.



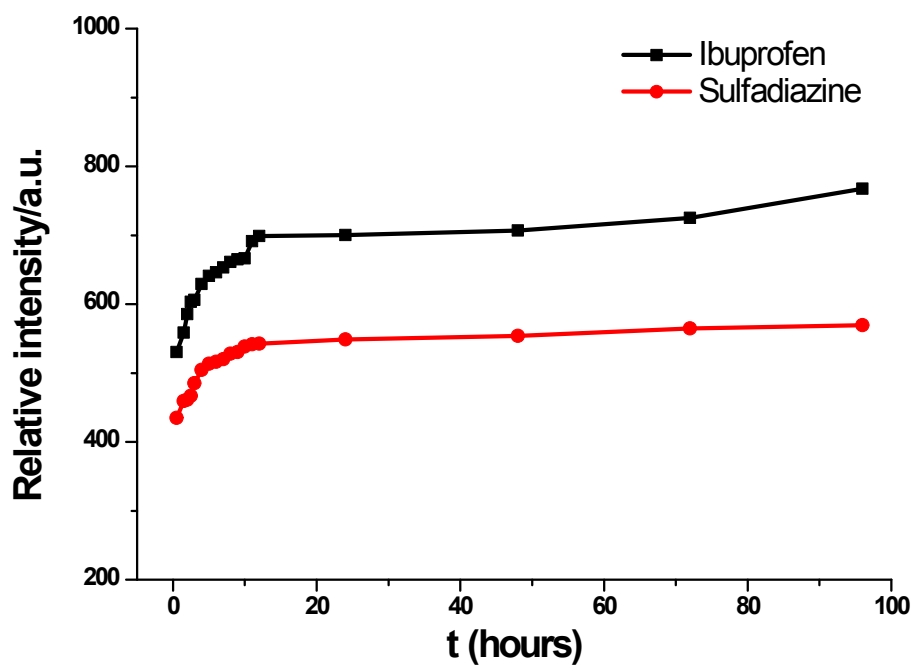
**Figure S17.** Release process of 5-FU from the drug-loaded **1** ( relative intensity vs. wavelength).



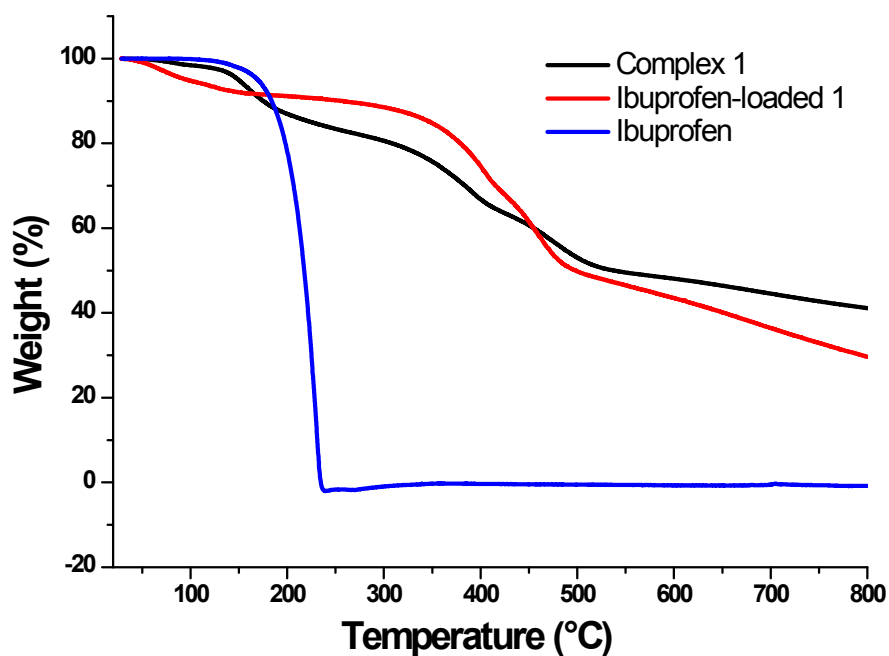
**Figure S18.** UV-vis absorption spectra of ibuprofen methanol solution before (black) and after (red) the interaction with **1** when diluted 250 times.



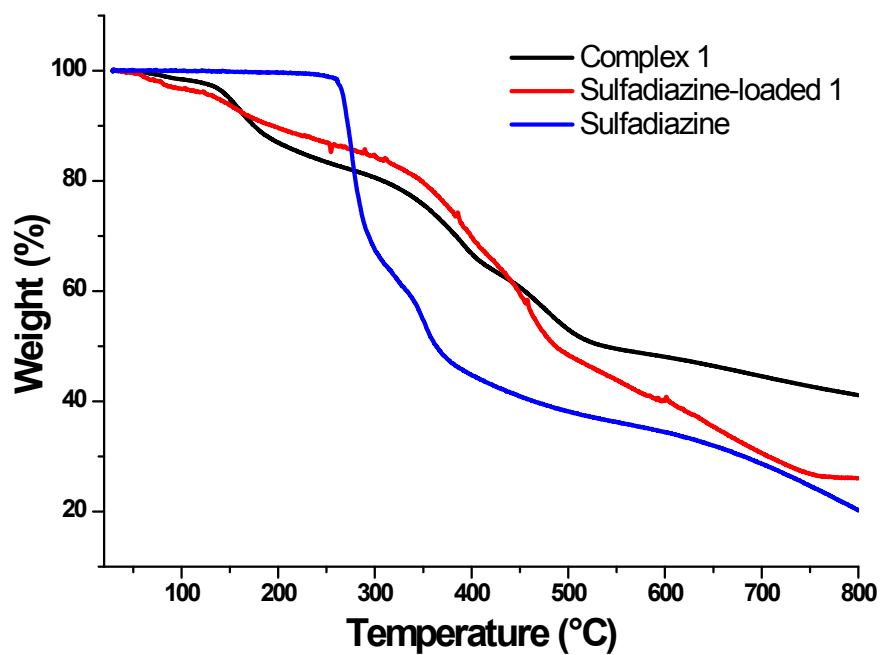
**Figure S19.** UV-vis absorption spectra of sulfadiazine methanol solution before (black) and after (red) the interaction with **1** when diluted 250 times.



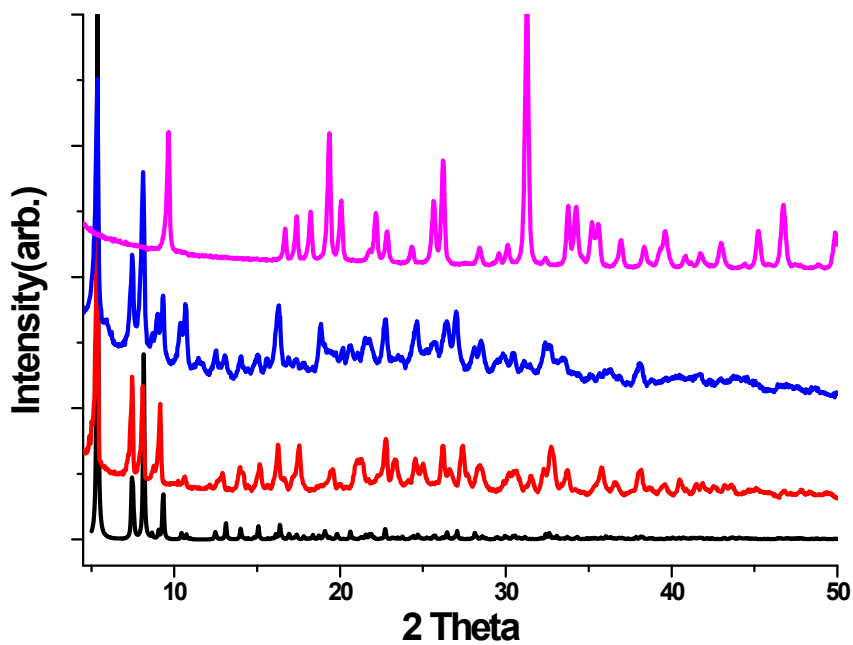
**Figure S20.** Release process of ibuprofen and sulfadiazine from the drug-loaded **1** (relative intensity vs. time).



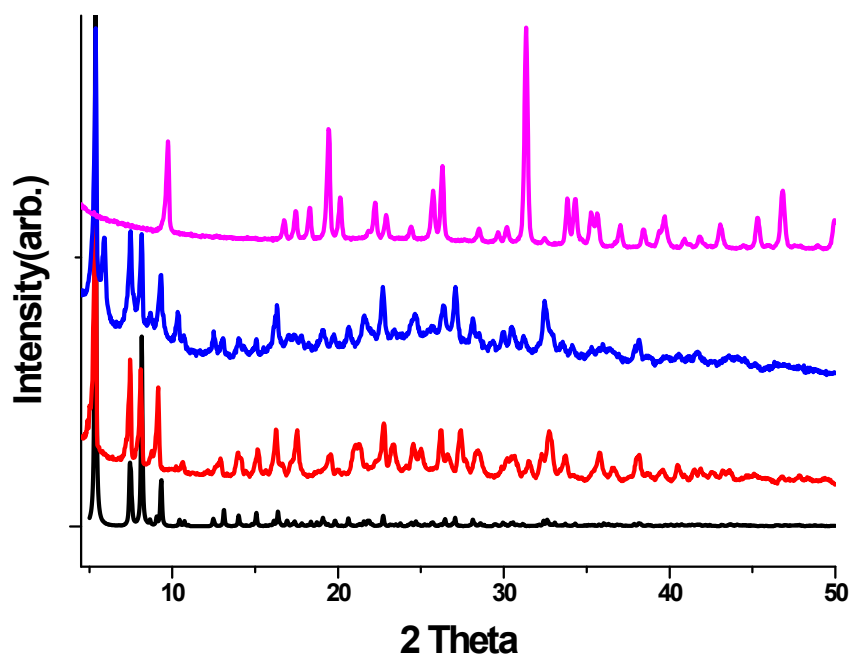
**Figure S21.** TGA curves of complex **1** (black); ibuprofen-loaded **1** (red); ibuprofen (blue).



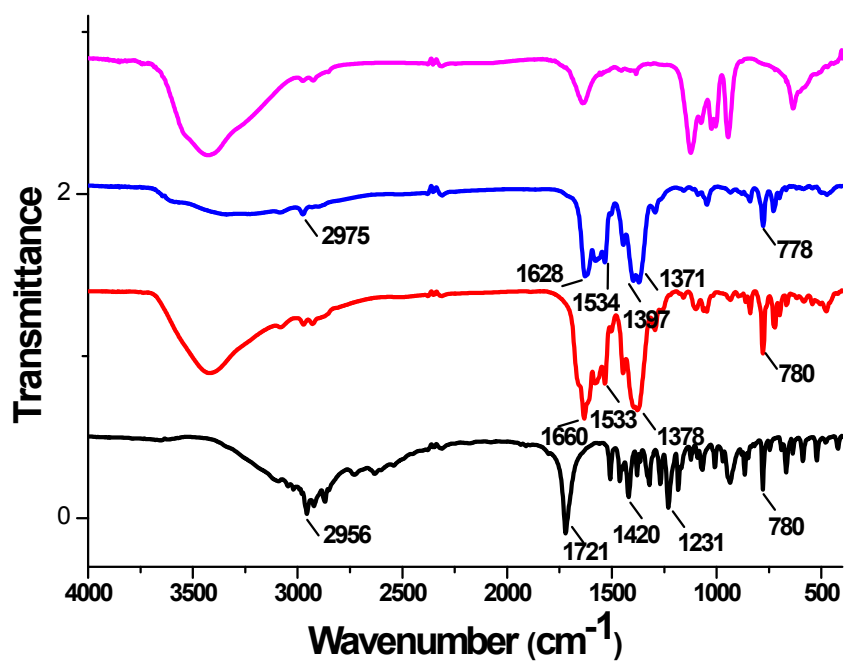
**Figure S22.** TGA curves of complex **1** (black); sulfadiazine-loaded **1** (red); sulfadiazine (blue).



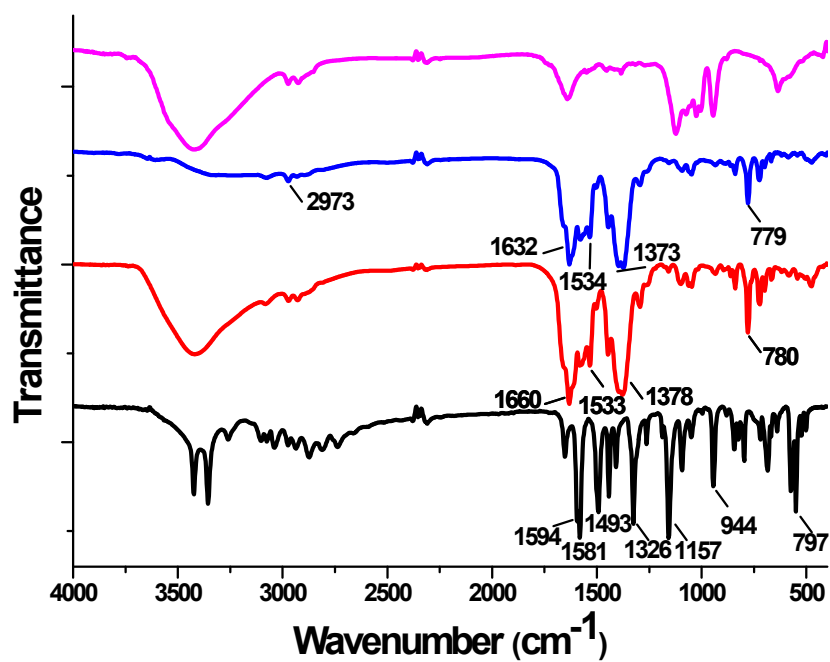
**Figure S23.** PXRD patterns for **1** (black, simulated; red, as-synthesized **1**; blue, ibuprofen-loaded **1**; pink, ibuprofen-released).



**Figure S24.** PXRD patterns for **1** (black, simulated; red, as-synthesized **1**; blue, sulfadiazine-loaded **1**; pink, sulfadiazine-released).



**Figure S25.** Infrared spectra of ibuprofen (black); complex **1** (red); ibuprofen-loaded **1** (blue); ibuprofen-released **1** (pink).



**Figure S26.** Infrared spectra of sulfadiazine (black); complex **1** (red); sulfadiazine-loaded **1** (blue); sulfadiazine-released **1** (pink).