

## Electronic Supporting Information

# A highly selective G-quadruplex-based luminescent switch-on probe for the detection of nanomolar strontium(II) ion in sea water

Ka-Ho Leung,<sup>‡a</sup> Victor Pui-Yan Ma,<sup>‡a</sup> Hong-Zhang He,<sup>a</sup> Daniel Shiu-Hin Chan,<sup>a</sup> Chung-Hang Leung<sup>bc</sup> and Dik-Lung Ma<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China.

E-mail: edmondma@hkbu.edu.hk

<sup>b</sup> State Key Laboratory of Quality Research in Chinese Medicine, University of Macau, Macao SAR, China

<sup>c</sup> Institute of Chinese Medical Sciences, University of Macau, Macao SAR, China.

## Experimental section

**Materials.** Reagents were purchased from Sigma Aldrich and used as received. Iridium chloride hydrate (IrCl<sub>3</sub>.xH<sub>2</sub>O) was purchased from Precious Metals Online. All oligonucleotides were synthesized by Techdragon Inc. (Hong Kong, China)

DNA sequences:

	Sequence
T2	5'-G <sub>4</sub> T <sub>2</sub> G <sub>4</sub> T <sub>2</sub> G <sub>4</sub> T <sub>2</sub> G <sub>4</sub> -3'
T2m1	5'-GCAGT <sub>2</sub> GCAGT <sub>2</sub> GCAGT <sub>2</sub> GCAG-3'
T2m2	5'-GAAGT <sub>2</sub> GAAGT <sub>2</sub> GAAGT <sub>2</sub> GAAG-3'

**General experimental.** Mass spectrometry was performed at the Mass Spectroscopy Unit at the Department of Chemistry, Hong Kong Baptist University, Hong Kong (China). Melting points were determined using a Gallenkamp melting apparatus and are uncorrected. Deuterated solvents for NMR purposes were obtained from Armar and used as received.

<sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C). <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced internally to solvent shift (CD<sub>3</sub>CN: <sup>1</sup>H, δ 1.94, <sup>13</sup>C δ 118.7; d<sub>6</sub>-DMSO: <sup>1</sup>H δ 2.50, <sup>13</sup>C δ 39.5). Chemical shifts (δ) are quoted in ppm, the downfield direction being defined as positive. Uncertainties in chemical shifts are typically ±0.01 ppm for <sup>1</sup>H and ±0.05 for <sup>13</sup>C. Coupling constants are typically ± 0.1 Hz for <sup>1</sup>H-<sup>1</sup>H and ±0.5 Hz for <sup>1</sup>H-<sup>13</sup>C couplings. The following abbreviations are used for convenience in reporting the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All NMR data was acquired and processed using standard Bruker software (Topspin). Emission spectra were recorded on a PTI QM4 spectrometer..

## Synthesis of [Ir(ppy)<sub>2</sub>(biq)]PF<sub>6</sub>

The following complexes were prepared according to the reported literature method, the precursor complex [Ir<sub>2</sub>(ppy)<sub>4</sub>Cl<sub>2</sub>],<sup>1</sup> and [Ir(ppy)<sub>2</sub>(biq)]PF<sub>6</sub> (**1**),<sup>3</sup> and characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HRMS.

## **1 as molecular probe for oligonucleotide based Sr<sup>2+</sup> detection**

5 μM of oligonucleotides (T2 or mutants) and indicated concentrations of Sr<sup>2+</sup> ion were added into Tris-HCl buffer (20 mM Tris, pH 7.0). The solutions were heated to 95 °C for 10 min, and were cool to room temperature at 0.1 °C/s.

The pre-annealed solution was added into 400 μL Tris-HCl buffer followed by addition of complex **1** at a final concentration of 2 μM. Emission spectra were recorded in the 550–750 nm range, after equilibration at 25.0 °C for 10 min. Excitation wavelength = 390 nm.

### **Assay selectivity**

5 μM of oligonucleotides (T2) and 10 μM of each ion (total 12 ions classified in three groups) were added into Tris-HCl buffer (20 mM Tris, pH 7.0) to make up a total volume of 100 μL. The solutions were heated to 95 °C for 10 min, and were cool to room temperature at 0.1 °C/s.

The pre-annealed solution was added into 400 μL Tris-HCl buffer followed by the addition of complex **1** at a final concentration of 2 μM. Emission spectra were recorded in the 550–750 nm range, after equilibration at 25.0 °C for 10 min. Excitation wavelength = 390 nm.

### **Real sample analysis**

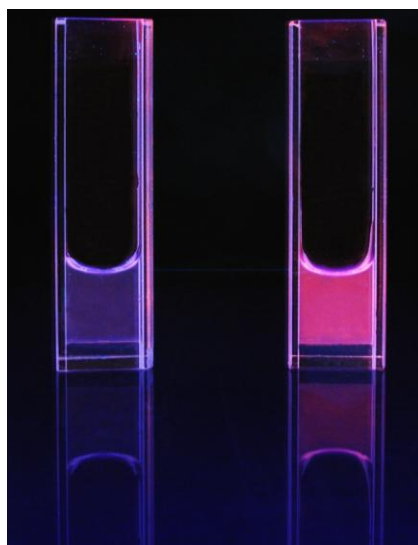
Sea water samples collected from Lamma Island, Hong Kong were pretreated using a syringe filter to remove particulate impurities. Indicated concentrations of Sr<sup>2+</sup> were then spiked into the water samples (100 μL). 5 μM of T2 was added into the sea water samples. The resulting solutions were heated to 95 °C for 10 min, and were cool to room temperature at 0.1 °C/s.

The pre-annealed water sample was added into 400 μL Tris-HCl buffer followed by the addition of complex **1** at the final concentration of 2 μM. Emission spectra were recorded in the 550–750 nm range, after equilibration at 25.0 °C for 10 min. Excitation wavelength = 390 nm.

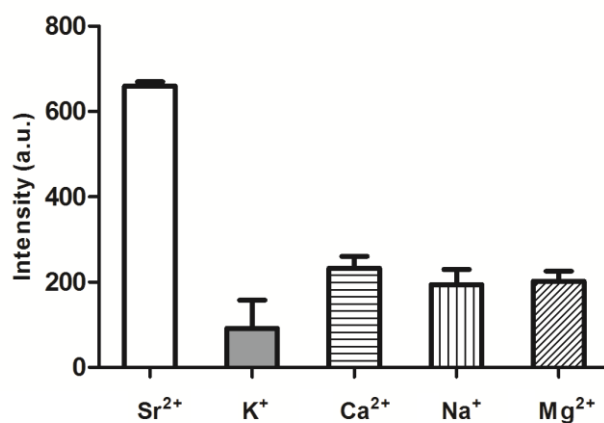
## **References**

1. M. S. Lowry, W. R. Hudson, R. A. Jr. Pascal and S. Bernhard, *J. Am. Chem. Soc.*, **2004**, *126*, 14129–14135.
2. H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu and S.-M. Peng, *J. Am. Chem. Soc.*, **2008**, *130*, 3413–3419.

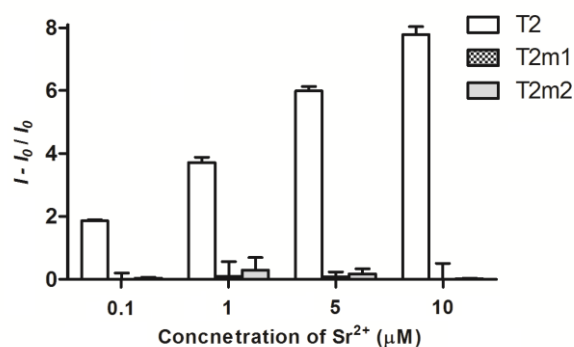
**Fig. S1** Photograph image of **1** and T2 (5  $\mu\text{M}$ ) in Tris buffer (20 mM, pH 7.0) in the absence (left) or presence (right) of 10  $\mu\text{M}$   $\text{Sr}^{2+}$  ions.



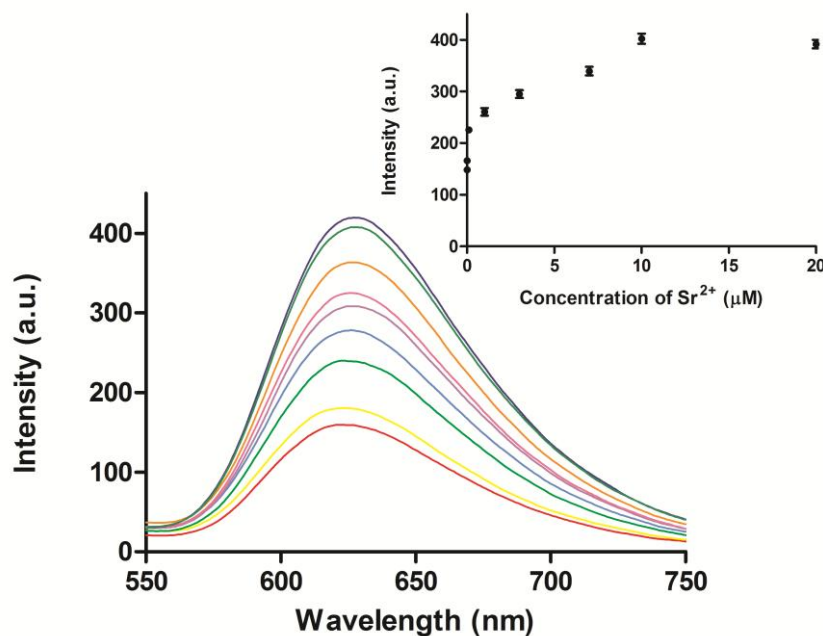
**Fig. S2** Intensity of complex **1** (2  $\mu\text{M}$ ) and T2 (5  $\mu\text{M}$ ) in the presence of  $\text{Sr}^{2+}$  ions (5  $\mu\text{M}$ ) or 100-fold excess of common ions in sea water ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ). Error bars represent the standard deviations of the results from three independent experiments.



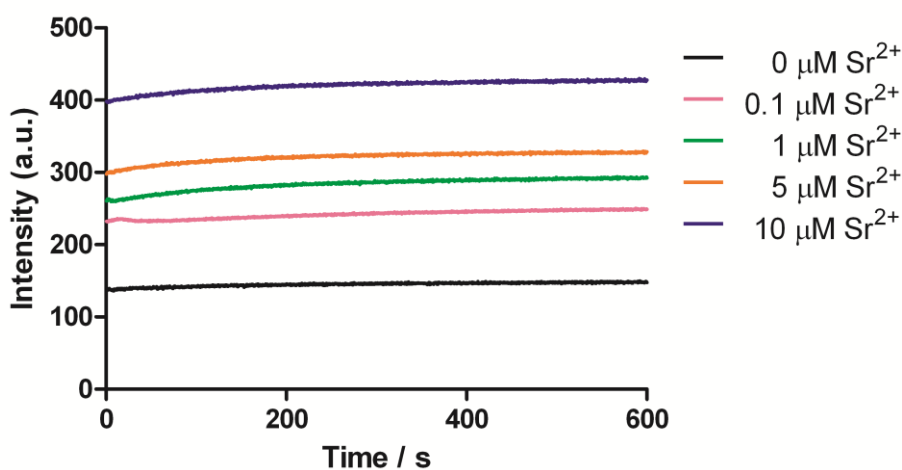
**Fig. S3** Relative luminescence intensity of complex **1** (2  $\mu\text{M}$ ) in the presence of  $\text{Sr}^{2+}$  ions (0.1, 1, 5 and 10  $\mu\text{M}$ ) and T2 or T2 mutants (5  $\mu\text{M}$ ). Error bars represent the standard deviations of the results from three independent experiments.



**Fig. S4**  $\text{Sr}^{2+}$  ion determination in sea water sample collected from Lamma Island, Hong Kong.  $\text{Sr}^{2+}$  ions (0.01, 0.1, 1, 3, 7, 10 and 20  $\mu\text{M}$ ) were spiked into sea water samples, and the emission spectra were recorded with complex **1** (2  $\mu\text{M}$ ) and T2 (5  $\mu\text{M}$ ). Inset: Change in intensity at  $\lambda = 638 \text{ nm}$  versus  $\text{Sr}^{2+}$  concentration in sea water samples. Error bars represent the standard deviations of the results from three independent experiments.



**Fig. S5** Time course of luminescence response of the system which contains various concentrations of  $\text{Sr}^{2+}$  (0–10  $\mu\text{M}$ ) and T2 (5  $\mu\text{M}$ ) in diluted sea water sample upon addition of **1** (2  $\mu\text{M}$ ) at 25 °C.



**Table S1.** Comparison of detection limit and range for some recently reported analytical techniques for  $\text{Sr}^{2+}$  ions. References refer to those in the main text.

Method	Detection limit	Range	Analyte	Ref.
Functionalized gold nanoparticles	7 $\mu\text{M}$	7–20 $\mu\text{M}$	$\text{Ca}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$	8
Potentiometric membrane sensor	240 nM	240 nM–100 $\mu\text{M}$	$\text{Sr}^{2+}$	10b

PVC-membrane sensor	550 nM	550 nM–100 $\mu$ M	Sr <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> +	10c
Ion-selective electrode	75 nM	75 nM–100 $\mu$ M	Sr <sup>2+</sup>	7b
G-quadruplex-based fluorescence assay	10 nM	10 nM–100 $\mu$ M	Sr <sup>2+</sup>	16
Ion-imprinted Au NPs composites and SPR spectroscopy	20 fM	20 fM–100 pM	Alkaline-earth ions	9
Method in this study	13 nM	13 nM–10 $\mu$ M	Sr <sup>2+</sup>	