RSC Advances

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A G-quadruplex-based platform for the detection of Hg^{2+} ions using a luminescent iridium(III) complex†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We report herein the synthesis of a series of cyclometallated iridium(III) complexes as luminescent G-quadruplex-selective probes, which were used to construct an oligonucleotide-based platform for the dual detection and removal of Hg^{2+} ions.

Mercury ion (Hg^{2+}) is a highly toxic and hazardous pollutant in the environment that can accumulate in living organisms, particularly in aquatic lifeforms. This ion causes a number of severe health problems in humans, such as central nervous system and endocrine system damage, kidney failure and motion disorders.[1, 2] As a consequence, the development of analytical methods to detect Hg^{2+} ions in aqueous media is an important challenge.[3-5]

Existing analytical methods for the sensitive detection of Hg^{2+} ions include atomic absorption/emission spectroscopy (AAS/AES),[6] inductively-coupled plasma mass spectrometry (ICP-MS) and ion-selective electrodes.[7, 8] However, these methods generally require the use of expensive instrumentation and tedious preparation protocols, thus limiting the scope of their application. Ono and co-workers have reported the coordinative interaction between Hg^{2+} and thymine nucleobases,[9-12] sparking the development of oligonucleotide-based luminescent,[13-36] colorimetric,[18, 37-48] electrochemical[49, 50] and surface-enhanced Raman scattering[51] methods for Hg^{2+} ion detection.[52-55] For example, an electrochemiluminescence assay for the detection of Hg^{2+} ions was reported by Xu and co-workers.[36] However, many of these methods utilized relatively expensive labelled oligonucleotides,[14, 16, 17, 20, 25-28, 30, 35, 50, 56] or provided only a switch-off mode of detection.[13, 14] Furthermore, systems employing duplex DNA as an Hg^{2+} ion probe may be more susceptible to interference from exogenous DNA species present in the sample matrix.[15, 18, 19, 21, 23, 24, 29]

The G-quadruplex is a DNA secondary structure formed from guanine-rich sequences, and consists of square-planar arrangements of guanine nucleobases stabilized by Hoogsteen hydrogen bonding and monovalent cations.[57-59] The G-quadruplex motif has been widely used for the construction of analytical detection platforms due to its rich structural polymorphism.[26, 52, 53, 60-69] Meanwhile, luminescent metal

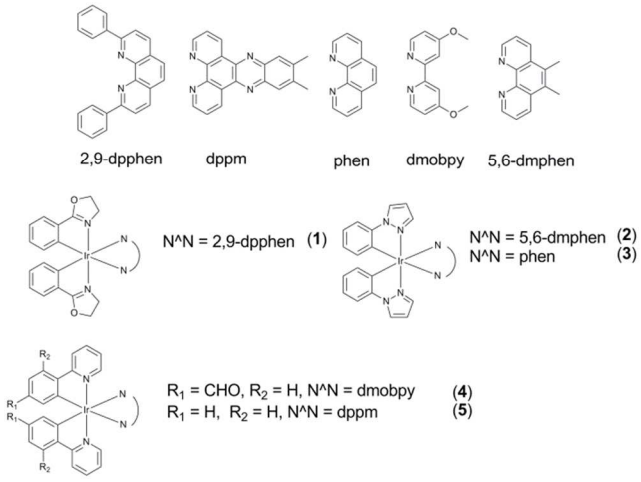
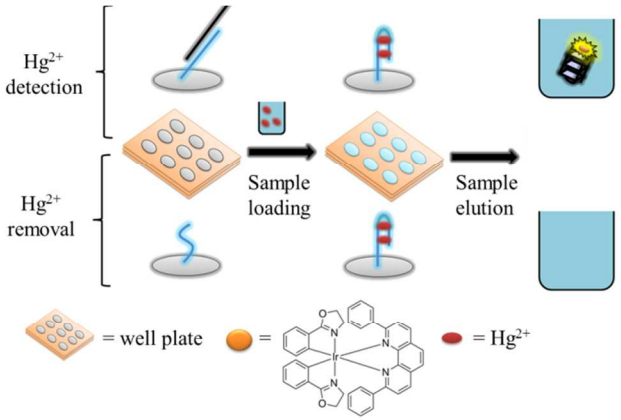


Fig. 1 Chemical structures of cyclometallated iridium(III) complexes **1**–**5**.

complexes have attracted tremendous interest in sensory applications due to their long-lived phosphorescence that can be readily distinguished from a short-lived auto-fluorescence background, their large Stokes shifts which prevent self-quenching, and their modular synthesis which allows their properties to be readily tuned without labor-intensive synthetic protocols.[35, 68, 70-74] In this work, we report herein the synthesis of a series of cyclometalated luminescent iridium(III) complexes as G-quadruplex-selective probes, which were used to construct an oligonucleotide-based platform for the luminescent detection of Hg^{2+} ions. Moreover, the application of the system for the removal of Hg^{2+} ions is presented as a proof-of-concept.

The mechanism of the proposed assay is depicted in Scheme 1. Initially, a G-quadruplex-forming sequence (black line) is hybridised to its partially complementary, thymine-containing sequence (blue line), which is immobilized on the surface of the well. The addition of Hg^{2+} ions promotes the formation of T-Hg^{2+}-T mismatches in the immobilized sequence, thus liberating the G-quadruplex-forming sequence into solution. The formation of the nascent G-quadruplex structure is then detected by the G-quadruplex-selective iridium(III) complex with a luminescent response.



Scheme 1. Schematic representation of the G-quadruplex-based luminescence sensing platform for Hg^{2+} ion detection and removal.

In the present study, five iridium(III) complexes (**1**–**5**, Fig. 1) were screened for their ability to selectively distinguish G-quadruplex (G4) DNA from double-stranded DNA (dsDNA) and single-stranded DNA (ssDNA) by testing their luminescence responses towards various forms of DNA. The cyclometallated iridium(III) complex **1** emerged as the top candidate, as it possessed the highest I_{G4}/I_{dsDNA} ratios out of the five complexes tested (Fig. S1), and also generated the highest luminescence response towards G-quadruplex DNA. A *ca.* 12-fold enhancement was observed in the luminescence signal of complex **1** at 5 μM of PS2.M G-quadruplex DNA. On the other hand, the addition of ssDNA or dsDNA (ds17) did not induce significant changes in the luminescence emission of complex **1** (Table S1, Fig. 2b). We presume that the enhanced luminescence of the complex **1** in the presence of G-quadruplex DNA was due to the selective interaction of complex **1** to the G-quadruplex. This shields the metal centre from solvent interactions and suppresses non-radiative decay of the excited state, thus enhancing its ^{3}MLCT emission. On the other hand, complex **1** did not interact significantly with dsDNA or ssDNA, thereby resulting in a weaker luminescence response. We also hypothesize that the other complexes do not possess the appropriate structures to selectively bind to G-quadruplex DNA, thus giving lower I_{G4}/I_{dsDNA} ratios compared to complex **1**.

Fluorescence resonance energy transfer (FRET) melting assays and G-quadruplex fluorescent intercalator displacement (G4-FID) assays were employed to further validate the suitability of complex **1** as a G-quadruplex-selective probe. Although the emission region of thiazole orange (TO) (510−750 nm) and complex **1** (500−700 nm) overlap, complex **1** is not expected to interfere in the G4-FID assay due to its very low absorbance at the excitation wavelength of TO (501 nm). The results of the G4-FID assay indicated that complex **1** could displace TO from G-quadruplex structures with $^{G4}DC_{50}$ values (half-maximal concentration of compound required to displace 50% TO from DNA) of 1.6 μM, while the displacement of TO from dsDNA was below 50% even at the highest concentration of **1** tested (Fig. 2c). The selectivity of complex **1** towards G-quadruplex DNA was further investigated by FRET-melting assays. The melting temperature (ΔT_m) of the F21T G-quadruplex was increased by about 11 °C upon the addition of 5 μM of complex **1** (Fig. 2d). By comparison, only a 3 °C increase in the melting temperature

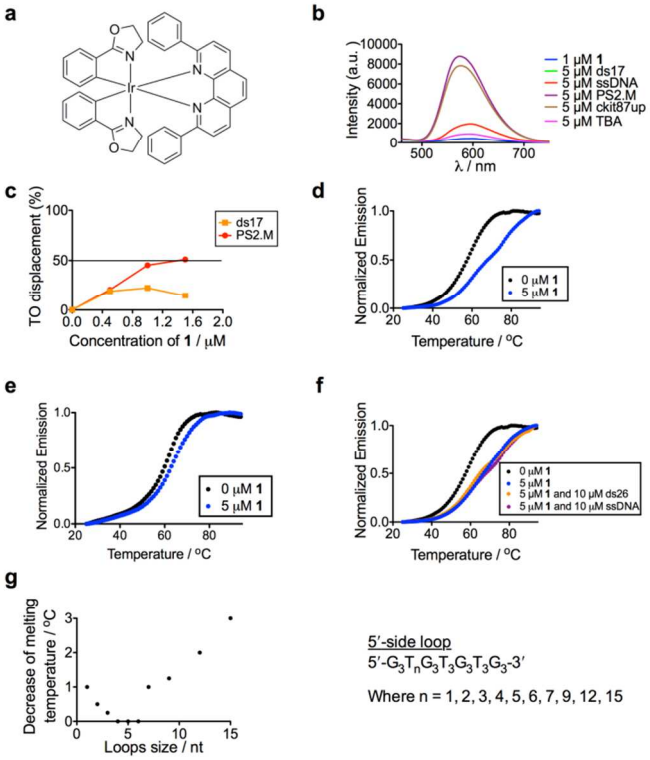


Fig. 2 (a) Chemical structure of complex **1**. (b) Emission spectrum of complex **1** (1 μM) in the presence of 5 μM of ssDNA, ds17 or various G-quadruplexes. (c) G4-FID titration curves of complex **1** with duplex (ds17) or G-quadruplex (PS2.M) DNA. (d) Melting profile of F21T G-quadruplex DNA (0.2 μM) in the absence and presence of **1** (5 μM). (e) Melting profile of F10T dsDNA (0.2 μM) in the absence and presence of **1** (5 μM). (f) Melting profile of F21T G-quadruplex DNA (0.2 μM) in the absence and presence of **1** (5 μM) and ds26 (10 μM) or ssDNA (10 μM). (g) Competitive FRET-melting assay results for complex **1** in the presence of G-quadruplexes with different loop lengths as the competitor. The decrease of melting temperature shown as a function of 5′-side loop size.

of F10T dsDNA was observed under the same conditions (Fig 2e). Furthermore, the addition of a 50-fold higher concentration of unlabeled competitor dsDNA (ds26) or ssDNA did not perturb the stabilizing effect of complex **1** towards the F21T G-quadruplex (Fig. 2f). Taken together, these results indicate that complex **1** binds selectively to G-quadruplex DNA over dsDNA or ssDNA.

Interestingly, complex **1** showed strong luminescence enhancement in the presence of PS2.M and c-kit87up G-quadruplexes, but only weak luminescence enhancement in the presence of the TBA G-quadruplex (Fig. 2b). TBA has previously been shown to readily accommodate planar aromatic ligands, but not ribbon-like molecules.[75] This result suggests that complex **1** may bind outside the G-tetrad for the other G-quadruplexes.[76] To examine the role of the G-quadruplex loops in the binding interaction of complex **1**, we investigated the relative binding affinity of complex **1** towards various G-quadruplex DNA structures with different loop sizes by a competitive FRET-melting assay. The G-quadruplex topologies of the sequences utilized in this experiment have been extensively validated by Mergny *et al.*[77] In this study, we found that the change in melting temperature decreased as the loop size was increased from 1 to 6

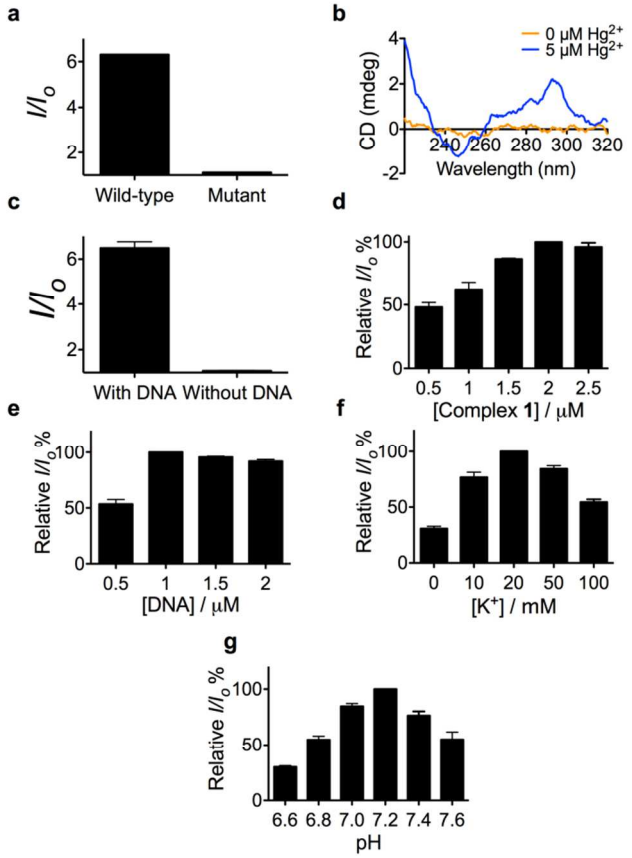


Fig. 3 (a) Luminescence of the system in the presence of wild-type and mutant G-quadruplex DNA (1 μM). (b) Circular dichroism (CD) spectra with and without 5 μM Hg^{2+} recorded in Tris buffer (50 mM Tris, pH 7.0). (c) Luminescence enhancement of the system in response to Hg^{2+} ions (50 nM) in the presence or absence of hairpin DNA (2 μM). (d) Relative luminescence intensity of the system with different concentrations of **1** (0.5, 1, 1.5, 2 and 2.5 μM). (e) Relative luminescence intensity of the system with different concentrations of DNA (0.5, 1, 1.5 and 2 μM). (f) Relative luminescence intensity with different concentrations of KCl (0, 10, 20, 50, and 100 mM). (g) Relative luminescence intensity with different pH (6.6, 6.8, 7.0, 7.2, 7.4 and 7.6). Unless otherwise stated, the concentration of complex **1** was 1 μM and the concentration of DNA was 1 μM.

nucleotides, but then increased again as the loop size was increased beyond 6 nucleotides (Fig. 2g). The result suggests that the G-quadruplex loop may play an important role in the G-quadruplex-**1** interaction, which is consistent with previous work by Qu and co-workers who showed that the nature of the loop region could affect the binding interaction between ligands and G-quadruplex DNA.[78]

Encouraged by the selective luminescence response of **1** to G-quadruplex DNA, we sought to employ **1** as a luminescent G-quadruplex probe for the detection of Hg^{2+} as described in Scheme 1. In the absence of Hg^{2+} ions, complex **1** was only slightly emissive as the G-quadruplex-forming sequence remained hybridized to its partially complementary, immobilized sequence, and no DNA was eluted into solution. However, the luminescence signal of **1** was significantly enhanced by *ca.* 6-fold in the presence of Hg^{2+} ions (Fig. 3a), presumably due to the formation of T-Hg^{2+}-T mismatches in the immobilized DNA sequence and the subsequent release of the G-quadruplex-forming sequence that interacted strongly with **1**. In contrast, the

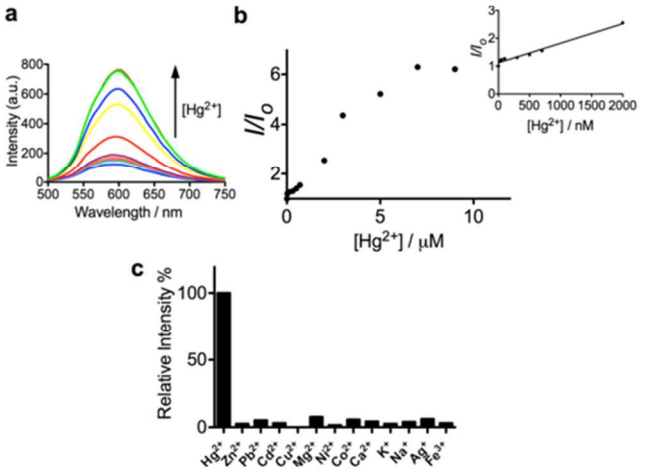


Fig. 4 (a) Emission spectra of the system ([**1**] = 2 μM, [DNA] = 1 μM, [K^+] = 20 mM) in the presence of increasing concentrations of Hg^{2+} ions. (b) Luminescence response of the system at λ = 604 nm *vs.* Hg^{2+} ion concentration. Inset: linear plot of the change in luminescence intensity at λ = 604 nm *vs.* Hg^{2+} ion concentration. (c) Relative luminescence intensity of the system ([**1**] = 2 μM, [DNA] = 1 μM) in the presence of 100 nM or 5-fold excess of other metal ions.

luminescence intensity of **1** was not significantly enhanced in response to Hg^{2+} ions when a mutant G-quadruplex sequence, which lacks consecutive guanine bases and is unable to fold into a G-quadruplex, was used (Fig. 3a). This result indicates that the formation of the G-quadruplex structure plays an important role in the mechanism of the Hg^{2+} sensing platform. Circular dichroism (CD) spectroscopy was also performed to validate the conformational change of DNA. In the absence of Hg^{2+} ions, no signal was observed in the CD spectrum of the eluted solution as the G-quadruplex-forming sequence remained hybridized to its immobilized sequence in the wells (Fig. 3a). However, when 5 μM of Hg^{2+} ions were added, a positive peak at 290 nm and negative peak at 250 nm appeared (Fig. 3b),[79] indicating that the G-quadruplex-forming DNA was released from the well surface and folded into an anti-parallel G-quadruplex structure. Moreover, no luminescence enhancement was observed in response to Hg^{2+} ions when DNA was absent, eliminating the possibility that complex **1** interacted directly with Hg^{2+} ions.

After optimization of the reaction conditions such as the concentrations of KCl, complex **1** and DNA, as well as pH (Fig. 3d–g), we investigated the luminescence response of the system to different concentrations of Hg^{2+} ion. Encouragingly, the luminescence signal of **1** was enhanced as the concentration of Hg^{2+} ion was increased. The luminescence of **1** plateaued at 7 μM Hg^{2+}, with *ca.* 6 fold enhancement in luminescent intensity, and experienced a slight decrease beyond this concentration (Fig. 4a and b). A detection limit of 25 nM was recorded using the 3σ method, indicating that the assay was highly sensitive for Hg^{2+} ions. The selectivity of this detection platform for Hg^{2+} over 12 other metal ions (K^+, Na^+, Ag^+, Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+} and Fe^{3+}) was also evaluated. The results showed that the luminescence response of the system for Hg^{2+} ions was significantly stronger than that for five-fold excess concentrations of the other metal ions (Fig. 4c).

Our sensing ensemble was applied for the detection of Hg^{2+}

ions in a natural water sample. A river water sample was collected from Nam Sang Wai River in Hong Kong and was diluted 10-fold using Tris buffer. Various concentrations of Hg^{2+} ions were then spiked into the sample. The results showed that the system experienced a gradual increase in luminescence intensity as the concentration of Hg^{2+} ions was increased (Fig. S3). This result demonstrates tht our detection platform could potentially be further developed as a sensitive probe for natural water sample analysis of Hg^{2+} ions.

To investigate the Hg^{2+} removal ability of our platform, we investigated the Hg^{2+} concentration of spiked natural water samples before and after loading into wells containing only the thymine-rich complementary sequence. The results showed that the Hg^{2+} concentration was reduced by 77% after the sample was loaded into the platform (Table S2). This result demonstrates the proof-of-concept of the Hg^{2+} removal ability of our platform.

In conclusion, we have synthesised a series of cyclometallated iridium(III) complexes as G-quadruplex-selective probes to construct a luminescent platform for the dual detection and removal of Hg^{2+} ions. The advantages of this method are the relatively low cost of the label-free approach, the switch-on mode of detection that reduces the chance of false positive signals, and the utilization of a G-quadruplex probe that could prevent interference from exogenous DNA species present in the sample matrix. This "mix-and-detect" methodology is simple, rapid, convenient to use and can detect down to 25 nM of Hg^{2+} ions. Furthermore, the potential application of the assay for monitoring and removing Hg^{2+} ions in a real water sample was demonstrated.

This work is supported by Hong Kong Baptist University (FRG2/13-14/008), Centre for Cancer and Inflammation Research, School of Chinese Medicine (CCIR-SCM, HKBU), the Health and Medical Research Fund (HMRF/13121482), the Research Grants Council (HKBU/201811, HKBU/204612, and HKBU/201913), the French National Research Agency/Research Grants Council Joint Research Scheme (A-HKBU201/12), the Science and Technology Development Fund, Macao SAR (103/2012/A3) and the University of Macau (MYRG091(Y2-L2)-ICMS12-LCH, MYRG121(Y2-L2)-ICMS12-LCH and MRG023/LCH/2013/ICMS).

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† Electronic Supplementary Information (ESI) available: experimental details and supplementary spectral data. See DOI: 10.1039/b000000x/

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We report herein the synthesis of a series of cyclometallated iridium(III) complexes as luminescent G-quadruplex-selective probes, which were used to construct an oligonucleotide-based platform for the dual detection and removal of Hg^{2+} ions.