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# Bichromophoric rhodamine-rhenium(I) and -iridium(III) sensory system: Synthesis, characterizations, photophysical and selective metal ions binding studies

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## ABSTRACT

A new class of rhenium(I) tricarbonyl diimine complexes containing rhodamine derivative as a sensory moiety, have been synthesized and characterized. Their photophysical and selective ion-binding properties have also been investigated, with the comparison of the previously reported cyclometalated iridium(III) system. One of the complex was found to exhibit selective binding toward Hg(II) ion with electronic absorption and emission spectral changes. On the other hand, the iridium(III) complexes were found to give similar electronic absorption response but different emission spectral changes upon addition of Hg(II) ion. Interestingly, efficient intramolecular energy transfer from rhodamine 6G to the cyclometalated iridium(III) moiety was suggested in one of the complexes, which could be modulated by selective ion-binding process upon ring-opening of rhodamine 6G. This report shows that the modification of rhodamine derivatives and the choice of transition metal ion could be important to influence the selective binding properties for development of colorimetric and/or luminescent probe.

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## 1. Introduction

There has been growing research interest in modification of luminescent probes for different metal ions since the pioneering work of crown ether by Pedersen in 1967 [1]. Host-guest chemistry has subsequently come to maturity by the work of macromolecules [1-4], such as cryptands, spherands and crown ethers, contributed by Lehn and Cram later on. After their endeavour to sensing chemistry, scientists have started to pay a great deal of attention to the development of luminescent sensors. Noelting et al. firstly documented the preparation of rhodamine derivatives [5]. As fluorophore and chromophore probes, rhodamine-based dyes have been widely used in the past several decades [6,7], owing to their great photo-stability and excellent spectroscopic properties, such as long excitation and emission wavelengths, large molar extinction coefficient and high fluorescence quantum yield, as well as the favorable solubility in water. Since the innovative work on the ring-opening behaviour of a rhodamine B derivative as a fluorescent chemosensor for copper(II) ion by Czarnik and

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http://dx.doi.org/10.1016/j.poly.2014.07.010 0277-5387/© 2014 Elsevier Ltd. All rights reserved. co-worker [8], the modification of rhodamine derivatives as chemosensors with high selectivity and sensitivity has been actively explored [9–19].

In view of the general limitations commonly encountered in organic fluorophores, such as high photobleaching rates, short fluorescence lifetimes and small Stokes' shifts, the search for new chromophores and luminophores to act as luminescent chemosensors continues. Transition-metal complexes were found to have a series of advantages for chemosensing, including longer luminescent lifetimes in the process of detection; kinetic inertness and photochemical stability; relatively high triplet quantum yields arising from the heavy metal effect; lower excitation energy required. Therefore, the design and utilization of transition metal-based luminescent chemosensors which commonly display phosphorescence lead to attractive alternatives that could fulfill roles that are complementary to those offered by organic fluorophores. Although there are a few reports on the combination of the rhodamine unit with another organic chromophore or luminophore in a single molecule [20,21], it is surprising to find that the related construction of bichromophoric array by the incorporation of a luminescent transition metal complex into a rhodamine derivative with sensory functionality is relatively unexplored [22,23]. Of particular interest to us is the possibility that incorporation of rhodamine derivative into a luminescent transition metal complex may allow access to a variety of new bichromophoric sensory systems. Therefore a program was initiated to design and synthesize different rhodamine-containing ligands and to coordinate them to the bichromophoric systems with the combination of various transition metal complexes and rhodamine-derivatives. Herein, we report to design and synthesize rhodamine-appended rhenium(I) tricarbonyl diimine complexes and their photophysical and selective ion-binding properties, with the comparison of the previously reported cyclometalated iridium(III) system [22].

#### 2. Experimental

#### 2.1. Materials

All the solvents for synthesis were of analytical grade. Methanol for analysis was of HPLC grade. Rhodamine 6G and rhodamine B base were purchased from Acros Organics Company. 4,4'-Dimethyl-2,2'-bipyridine, iridium(III) chloride hydrate, rhenium(I) pentacarbonyl bromide and ammonium hexafluorophosphate were purchased from Aldrich Chemical Company. Mercury(II) perchlorate, lead(II) perchlorate, copper(II) perchlorate, zinc(II) perchlorate, cadmium(II) perchlorate, barium(II) perchlorate, manganese(II) perchlorate, silver(I) perchlorate, potassium(I) perchlorate, sodium(I) perchlorate and lithium(I) perchlorate were purchased from Aldrich Chemical Company with purity over 99.0% and were used as received. Hydrazine monohydrate and ethylenediamine were purchased from Alfa Aesar Company. The precursors 4-methyl-4'-carbonyl-2,2'-bipyridine [24], rhodamine 6G hydrazide [25], rhodamine 6G ethylamine [25], rhodamine B hydrazide [26], rhodamine B ethylamine [26], and  $Ir_2(dpqx)_4Cl_2$  (dpqx = 2,3diphenylquinoxaline) [27] were synthesized according to the modification of literature methods.

## 2.2. Synthesis

**L1**: The mixture of rhodamine B hydrazide (0.456 g, 1 mmol) and 4-methyl-4'-carbonyl-2,2'-bipyridine (0.198 g, 1 mmol) in dichloromethane (15 ml) was heated to reflux for 12 h. The mixture was cooled to room temperature and the solvent was removed in vacuum to afford brown oil. Methanol was added to precipitate a white solid which was then filtered and washed with methanol. Yield: 0.56 g, 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4-</sub> Si)/ppm:  $\delta$  = 1.16 (t, I = 7.0 Hz, 12H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.41 (s, 3H, CH<sub>3</sub>) on bipyridyl ring), 3.32 (q, J = 7.0 Hz, 8H, N– $CH_2$ – $CH_3$ ), 6.24 (dd, J = 8.9, 2.6 Hz, 2H, xanthene protons), 6.47 (d, J = 2.5 Hz, 2H, xanthene protons), 6.54 (d, J = 8.8 Hz, 2H, xanthene protons), 7.12 (m, 2H, bipyridyl proton and phenyl proton on rhodamine), 7.48 (m, 2H, phenyl protons on rhodamine), 7.76 (dd, J = 5.2, 1.5 Hz, 1H, phenyl proton on rhodamine), 8.01 (dd, J = 6.2, 1.2 Hz, 1H, bipyridyl proton), 8.17 (m, 2H, bipyridyl proton and CH=N), 8.41 (s, 1H, bipyridyl proton), 8.51 (d, 1H, *J* = 5.0 Hz, bipyridyl proton), 8.58 (d, 1H, J = 5.1 Hz, bipyridyl proton); positive EI-MS, m/z: 637  $[M+H]^{+}$ .

*L***2**: The procedure was similar to that described for the synthesis of **L1** except rhodamine B ethylamine was used instead of rhodamine B hydrazide. Yield: 0.58 g, 87%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  1.16 (t, *J* = 7.0 Hz, 12H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.43 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.32 (q, *J* = 7.0 Hz, 8H, N–CH<sub>2</sub>–CH<sub>3</sub>), 3.50 (s, *J* = 2.8 Hz, 4H, N–CH<sub>2</sub>CH<sub>2</sub>–N), 6.25 (dd, *J* = 8.9, 2.6 Hz, 2H, xanthene protons), 6.47 (d, *J* = 2.5 Hz, 2H, xanthene protons), 7.11 (m, 2H, bipyridyl proton and phenyl proton on rhodamine), 7.43 (m, 2H, phenyl protons on rhodamine), 7.57 (m, 1H, phenyl proton on rhodamine), 7.91 (m, 1H, bipyridyl proton), 8.08 (s, 1H, CH=N), 8.21 (m, 1H, bipyridyl proton), 8.46 (m, 1H, bipyridyl proton), 8.53

(dd, *J* = 5.0, 0.8 Hz, 1H, bipyridyl proton), 8.66 (dd, *J* = 5.0, 0.8 Hz, 1H, bipyridyl proton); positive EI-MS, *m*/*z*: 665 [M+H]<sup>+</sup>.

**L3**: The procedure was similar to that described for the synthesis of **L1** except rhodamine 6G hydrazide was used instead of rhodamine B hydrazide. Yield: 0.59 g (98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  = 1.32 (t, *J* = 7.1 Hz, 6H, N–CH<sub>2</sub>–*CH*<sub>3</sub>), 1.87 (s, 6H, CH<sub>3</sub> on xanthene ring), 2.42 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.20–3.25 (m, 4H, N–*CH*<sub>2</sub>–CH<sub>3</sub>), 3.47–3.50 (m, 2H, NH), 6.35 (s, 2H, xanthene protons), 6.43 (s, 2H, xanthene protons), 7.06 (dd, *J* = 1.5 and 6.0 Hz, 1H, phenyl proton on rhodamine), 7.12 (dd, *J* = 0.8 and 4.9 Hz, 1H, bipyridyl proton), 7.45–7.52 (m, 2H, phenyl protons on rhodamine), 7.74 (dd, *J* = 1.4 and 5.1 Hz, 1H, bipyridyl proton), 8.15 (s, 2H, CH=N and bipyridyl proton), 8.25 (s, 1H, bipyridyl proton), 8.50 (d, *J* = 5.1 Hz, 1H, bipyridyl proton), 8.57 (d, *J* = 5.1 Hz, 1H, bipyridyl proton); positive EI-MS: *m/z*: 609 [M]<sup>+</sup>.

*L***4**: The procedure was similar to that described for the synthesis of **L3** except rhodamine 6G ethylamine was used instead of rhodamine 6G hydrazide. Yield: 0.52 g (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  = 1.31 (t, *J* = 7.1 Hz, 6H, N-CH<sub>2</sub>-*C*H<sub>3</sub>), 1.84 (s, 6H, CH<sub>3</sub> on xanthene ring), 2.44 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.19 (q, *J* = 7.1 Hz, 4H, N-*C*H<sub>2</sub>-*C*H<sub>3</sub>), 3.46-3.63 (m, 6H, NH and N-CH<sub>2</sub>CH<sub>2</sub>-N), 6.21 (s, 2H, xanthene protons), 6.35 (s, 2H, xanthene protons), 7.04 (dd, *J* = 2.1 and 5.1 Hz, 1H, phenyl proton on rhodamine), 7.14 (d, *J* = 0.6 and 4.9 Hz, 1H, bipyridyl proton), 7.41-7.48 (m, 2H, phenyl protons on rhodamine), 7.56 (dd, *J* = 1.4 and 5.0 Hz, 1H, bipyridyl proton), 7.92-7.96 (m, 2H, CH=N and phenyl proton on rhodamine), 8.21 (s, 1H, bipyridyl proton), 8.39 (s, 1H, bipyridyl proton), 8.54 (d, *J* = 5.0 Hz, 1H, bipyridyl proton); positive EI-MS: *m/z*: 637 [M]<sup>+</sup>.

[Re(CO)<sub>3</sub>(L1)Br] (1): This was synthesized by modification of a literature procedure [28]. A mixture of Re(CO)<sub>5</sub>Br (0.07 g, 0.17 mmol) and L1 (0.09 g, 0.17 mmol) in toluene (20 ml) was heated to reflux under N<sub>2</sub> in the dark for 4 h. The solvent was removed under reduced pressure. Subsequent recrystallization by vapour diffusion of diethyl ether into dichloromethane solution of products gave **1** as red-orange crystals. Yield: 121 mg, 72%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  1.16 (td, I = 7.1, 1.4 Hz, 12H, N-CH<sub>2</sub>-CH<sub>3</sub>), 2.64 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.41-3.25 (m, 8H, N-CH<sub>2</sub>-CH<sub>3</sub>), 6.26 (m, 2H, xanthene protons), 6.48 (m, 4H, xanthene protons), 7.34 (m, 2H, bipyridyl proton and phenyl proton on rhodamine), 7.58 (m, 2H, phenyl proton on rhodamine), 8.04 (m, 1H, phenyl proton on rhodamine), 8.10 (s, 1H, bipyridyl proton), 8.43 (s, 1H, bipyridyl proton), 8.73 (s, 1H, CH=N), 8.87 (m, 2H, bipyridyl protons); positive FAB-MS: *m*/*z*: 987.1 [M–H]<sup>+</sup>, 907.1 [M–Br]<sup>+</sup>; elemental *Anal*. Calc. for complex 1: C, 52.17; H, 4.34; N, 8.49. Found: C, 52.22; H, 4.27; N, 8.30%.

[*Re*(*CO*)<sub>3</sub>(*L2*)*Br*] (**2**): The procedure was similar to that described for the synthesis of **1** except **L2** was used instead of **L1**. Yield: 118 mg, 68%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ ppm:  $\delta$  1.17 (dt, *J* = 6.0 Hz, *J* = 3.0 Hz, 12H, N–CH<sub>2</sub>–*CH*<sub>3</sub>), 2.62 (s, 3H, *CH*<sub>3</sub> on bipyridyl ring), 3.29–3.36 (dq, *J* = 6.0 Hz, *J* = 3.0 Hz, 8H, N–*CH*<sub>2</sub>–*C*H<sub>3</sub>), 3.56 (m, 4H, *CH*<sub>2</sub>*CH*<sub>2</sub>), 6.25 (m, 2H, xanthene protons), 6.41 (m, 4H, xanthene protons), 7.09 (m, 1H, phenyl proton on rhodamine), 7.34 (m, 1H, bipyridyl proton), 7.45 (m, 3H, phenyl protons on rhodamine and bipyridyl proton), 7.90 (m, 1H, phenyl protons, 8.51 (m, 1H, bipyridyl proton), 8.88 (d, *J* = 5.7 Hz, 1H, bipyridyl proton), 9.03 (d, *J* = 5.6 Hz, 1H, bipyridyl proton), positive FAB-MS: *m/z* 1017.4 [M]<sup>+</sup>; elemental *Anal.* Calc. for complex **2**·H<sub>2</sub>O: C, 52.27; H, 4.45; N, 8.13. Found: C, 52.49; H, 4.10; N, 7.85%.

 $[Ir(dpqx)_2L3]PF_6$  (**3**): Complex **3** was obtained by the reaction of **L3** (38 mg, 0.06 mmol) with 0.5 equiv of dinuclear iridium(III) precursor complex,  $Ir_2(dpqx)_4Cl_2$  (50 mg, 0,03 mmol), in a solvent

mixture (30 ml) of dichloromethane and methanol (1:1 v/v) under reflux condition for 4 h. After removal of solvent in vacuum, the red solid residue was then dissolved in hot methanol. A saturated methanolic solution of ammonium hexafluorophosphate was added to precipitate the red solid. Subsequent recrystallization of the complexes by diffusion of diethyl ether vapour into a solution of the complex in dichloromethane afforded complex 3 as an orange solid: Yield: 57 mg, 60%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  = 1.24–1.29 (m, 6H, N–CH<sub>2</sub>–CH<sub>3</sub>), 1.83 (s, 6H, CH<sub>3</sub> on xanthene ring), 2.62 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.08-3.21 (m, 4H, N-CH2-CH3), 3.44-3.55 (m, 2H, NH), 6.20 (s, 1H, xanthene protons), 6.21 (s, 1H, xanthene protons), 6.37-6.43 (m, 4H, xanthene and 2,3-diphenylquinoxaline protons), 6.64-6.70 (m, 2H, 2,3-diphenylquinoxaline protons), 6.72-6.78 (m, 2H, 2,3-diphenylquinoxaline protons), 7.08-7.19 (m, 4H, 2,3-diphenylquinoxaline protons), 7.28-7.34 (m, 3H, phenyl protons on rhodamine and 2.3-diphenvlquinoxaline proton), 7.51–7.62 (m. 4H. phenyl proton on rhodamine and 2,3-diphenylquinoxaline protons), 7.67-7.71 (m, 6H, 2,3-diphenylquinoxaline protons), 7.75-7.78 (m, 4H, 2,3-diphenylquinoxaline and bipyridyl protons), 7.84 (d, J = 6.4 Hz, 2H, 2,3-diphenylquinoxaline protons), 7.91 (s, 1H, bipyridyl proton), 7.97-8.03 (m, 3H, phenyl proton on rhodamine and 2,3-diphenylquinoxaline protons), 8.07 (s, 1H, bipyridyl proton), 8.51-8.54 (m, 2H, CH=N and bipyridyl proton), 8.59 (d, J = 5.7 Hz, 1H, bipyridyl proton); positive ESI-MS: m/z: 1364.5  $[M-PF_6]^+$ ; elemental Anal. Calc. for  $C_{78}H_{62}F_6IrN_{10}O_2P\cdot 4H_2O$ : C, 59.26; H, 4.46; N, 8.86. Found: C, 59.08; H, 4.20; N, 8.79%.

 $[Ir(dpqx)_2L4]PF_6(4)$ : The procedure was similar to that described for the synthesis of 3 except L4 (40 mg, 0.06 mmol) was used instead of L3. Yield: 72 mg, 74%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si)/ppm:  $\delta$  = 1.26–1.31(m, 6H, N–CH<sub>2</sub>–CH<sub>3</sub>), 1.82 (s, 6H, CH<sub>3</sub> on xanthene ring), 2.59 (s, 3H, CH<sub>3</sub> on bipyridyl ring), 3.14-3.20 (m, 4H, N-CH<sub>2</sub>-CH<sub>3</sub>), 3.29 (t, J = 6.4 Hz, N-CH<sub>2</sub>), 3.49-3.62 (m, 4H, N-CH<sub>2</sub> and NH), 6.09 (s, 1H, xanthene protons), 6.12 (s, 1H, xanthene protons), 6.31 (s, 1H, xanthene protons), 6.33 (s, 1H, xanthene protons), 6.45 (t, J = 6.2 Hz, 2H, 2,3-diphenylquinoxaline protons), 6.68-6.72 (m, 2H, 2,3-diphenylquinoxaline protons), 6.75–6.80 (m. 2H, 2.3-diphenylquinoxaline protons), 7.04 (t, J = 4.2 Hz, 1H, 2,3-diphenylquinoxaline protons), 7.14–7.20 (m, 4H, 2,3-diphenylquinoxaline protons), 7.31-7.36 (m, 2H, phenyl protons on rhodamine), 7.42 (t, J = 4.2 Hz, 2H, phenyl protons on rhodamine), 7.54-7.60 (m, 3H, 2,3-diphenylquinoxaline protons), 7.67-7.69 (m, 6H, 2,3-diphenylquinoxaline protons), 7.82-7.87 (m, 5H, 2,3-diphenylquinoxaline and bipyridyl protons), 7.90 (s, 1H, CH=N), 7.98-8.02 (m, 2H, 2,3-diphenylquinoxaline protons), 8.05 (d, J = 5.7 Hz, 1H, bipyridyl proton), 8.25 (s, 1H, bipyridyl proton), 8.41 (s, 1H, bipyridyl proton), 8.52 (d, J = 5.6 Hz, 1H, bipyridyl proton), 8.62 (d, J = 5.6 Hz, 1H, bipyridyl proton); positive ESI-MS: m/z: 1390 [M-PF<sub>6</sub>]<sup>+</sup>; elemental Anal. Calc. for C<sub>80</sub>H<sub>66</sub>F<sub>6</sub>IrN<sub>10</sub>O<sub>2</sub>P: C, 62.53; H, 4.33; N, 9.11. Found: C, 62.49; H, 4.10; N, 8.85%.

#### 2.3. Physical measurements

All <sup>1</sup>H NMR spectra were obtained from a Bruker DPX 300 (300 MHz) or Bruker DPX 400 (400 MHz) Fourier-transform NMR spectrometers with chemical shifts, which were reported relative to tetramethylsilane,  $(CH_3)_4$ Si. Fast atom bombardment (FAB) and electron impact (EI) ionization spectra were obtained and Finnigan MAT95 mass spectrometer. All positive-ion electrospray ionization (ESI) spectra were performed on a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer. Elemental analyses of the complexes were carried out on a Carlo Erba 1106 elemental analyzer at the institute of Chemistry of the Chinese Academy of Sciences, Beijing, China. The UV–Vis absorption spectra were obtained by utilizing a Hewlett-Packard 8452A diode. Steady state excitation and emission spectra at room temperature were

recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. The emission spectroscopic investigations of all solution required a degassing procedure on a high-vacuum line in a degassing cell, which contains 10-ml Pyrex bulb and a 1-cm path length quartz cuvette and is sealed from the atmosphere by a Bibby Rotaflo HP6 Telflon stopper. At least four successive freeze-pump-thaw cycles were performed to degas the solutions prior to the measurement.

#### 2.4. Crystal structure determination

Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether vapor into a dichloromethane and acetone solutions of the complexes, respectively, for 1 and 4. After the structural solution and refinement, one ethyl substituent of amino group in **4** was found to be converted into hydrogen on the rhodamine moiety,  $\mathbf{4}'$  was accordingly denoted for such complex. The X-ray diffraction data were collected on a Bruker Smart CCD 1000 diffractometer using graphite monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Raw frame data of **4**' were integrated with SAINT [29] program. Semi-empirical absorption correction with SADABS [30] was applied. The crystal data and refinement details are listed in Table 1. The structure was solved by direct methods employing SHELXS-97 program [31]. Re, Br, Ir, P and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97 [32]. For 1, there was one formula unit in the asymmetric unit. Half of diethylether was located with O at the special position. For 4', there was one formula unit in the asymmetric unit. Two halves of PF<sub>6</sub> anions were located, in which P atoms locate at the special positions. Two acetone solvent molecules and one water O were located. Restrains were applied to the acetones, assuming O-C and C-C bond lengths of around 1.25(2) and 1.53(2) Å, respectively. Other solvent molecules could not be located reliably, so Platon-squeeze method was employed to abstract the influence of the unlocated solvent molecules. This gave rise to the potential solvent accessible void volume of 1094 Å<sup>3</sup> per unit cell, which corresponds to 137 electron counts per unit cell.

#### 2.5. Ion-binding studies

Binding constants for 1:1 complexation were determined by nonlinear least-squares fits to Eq. (1), in which the derivations were described previously [33].

$$X = X_0 + \frac{X_{\rm lim} - X_0}{2[M]_{\rm T}} \{ [M]_{\rm T} + [{\rm Hg}^{2+}] + 1/K_{\rm S} - [([M]_{\rm T} + [{\rm Hg}^{2+}] + 1/K_{\rm S})^2 - 4[M]_{\rm T}[{\rm Hg}^{2+}]]^{1/2} \}$$
(1)

where  $X_0$  and X are the absorbance (or luminescence intensity) of the rhenium(I) or iridium(III) complex at a selected wavelength in the absence and presence of the Hg(II) ion, respectively,  $[M]_T$  is the total concentration of the rhenium(I) or iridium(III) complex,  $[Hg^{2+}]$  is the concentration of the Hg(II) ion,  $X_{lim}$  is the limiting value of absorbance (or luminescence intensity) in the presence of excess Hg(II) ion and  $K_s$  is the stability constant.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

The preparation of **L3**, **L4**, **3** and **4** has been communicated recently [22]. The synthetic pathways of the rhodamine deriva-

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#### Table 1

Crystal and structure determination data of **1** and **4**'.

Complex	1	4′
Empirical formula	C <sub>43</sub> H <sub>40</sub> BrN <sub>6</sub> O <sub>5</sub> Re. <sup>1</sup> / <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> O)	C <sub>82</sub> H <sub>72</sub> F <sub>6</sub> IrN <sub>10</sub> O <sub>5</sub> P
Formula weight	1023.98	1614.67
T (K)	301(2)	301(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	C2/c	$\bar{P}$
a (Å)	25.488(6)	17.274(2)
b (Å)	12.781(3)	18.135(2)
c (Å)	28.862(6)	18.443(2)
α (°)	90	115.72(1)
$\beta$ , (°)	98.14(2)	114.62(1)
γ (°)	90	94.54(1)
V	9307(4)	4487.1(9)
$Z(Å^3)$	8	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.462	1.195
Crystal size, $mm \times mm \times mm$	$0.300.25 \times 0.15$	0.48  imes 0.13  imes 0.11
Theta range for data collection (°)	1.79–25.68	1.70-25.68
Index ranges	$-31 \leq h \leq 31$	$-21 \leqslant h \leqslant 21$
	$-14 \leqslant k \leqslant 15$	$-22 \leqslant k \leqslant 22$
	$-34 \leq l \leq 35$	$-22 \leqslant l \leqslant 22$
Reflections collected/unique	26856/8786	46816/16984
Completeness to theta = $25.68^{\circ}$ (%)	99.4	99.6
Goodness-of-fit (GOF) on $F^2$	1.039	1.073
Final R indices <sup>a</sup> $[I > 2\sigma(I)]$	$R_1 = 0.0448$	$R_1 = 0.0408$
	$wR_2 = 0.1260$	$wR_2 = 0.1236$
Largest different peak and hole (e Å <sup>-3</sup> )	1.378 and -1.020	1.467 and -0.825

<sup>a</sup>  $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2], R_1 = \Sigma ||F_o| - |F_c|| / \Sigma ||F_o| \text{ and } wR_2 = \{ [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2] \}^{1/2}.$ 



Scheme 1. Synthesis of L1-L4.

tive-containing bipyridine ligands, L1-L4, are summarized in Scheme 1. Ligands L1-L4 were similarly prepared from the condensation reaction of 4-carboxaldehyde-4'-methyl-2,2'-bipyridine with the corresponding rhodamine derivative hydrazide and ethylamine intermediates in methanol in reflux condition under nitrogen atmosphere for 5 h. The syntheses of complexes 1-4 are outlined in Scheme 2. Rhenium(I) tricarbonyl diimine complexes 1 and 2 were synthesized in good yield through the incorporation of rhodamine-appended bipyridine ligands, L1 and L2, into the precursor complex, [Re(CO)<sub>5</sub>Br], in reflux condition under an inert atmosphere of nitrogen in toluene. Reaction of L3 and L4 with 0.5 equivalent of dinuclear iridium(III) precursor complex, Ir<sub>2</sub>(dpqx)<sub>4</sub> Cl<sub>2</sub> (dpqx = 2,3-diphenylquinoxaline) [27], followed by metathesis with NH<sub>4</sub>PF<sub>6</sub> afforded the rhodamine derivative-containing iridium(III) complexes, 3 and 4 in reasonable yield. The identities of complexes 1-4 were confirmed by <sup>1</sup>H NMR spectroscopy, satisfactory elemental analyses and positive-ion FAB or ESI mass spectrometric methods. For <sup>1</sup>H NMR measurement, the complexes appended with rhodamine moieties (rhodamine 6G or rhodamine B) show triplet or multiplet signals in the range of  $\delta$  1.14–1.41

and quartet or multiplet signals in the range of  $\delta$  3.13–3.54, which can be assigned as N–CH<sub>2</sub>–CH<sub>3</sub> and N–CH<sub>2</sub>–CH<sub>3</sub> of the rhodamine moieties, respectively. Rhodamine 6G-containing complexes **3** and **4** have unique singlet signals at about  $\delta$  1.82, which can be referred to CH<sub>3</sub> on the xanthene ring of the rhodamine 6G. However, the absence of these signals was noted in the <sup>1</sup>H NMR spectra of complexes **1** and **2**, which were appended with rhodamine B derivative.

### 3.2. X-ray crystal structure

Single crystals of **1** suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether vapor into a dichloromethane solution. Although single crystals were obtained by slow diffusion of diethyl ether vapor into an acetone solution of **4**, one ethyl substituent of amino group in **4** was found to be converted into hydrogen on the rhodamine moiety after the structural solution and refinement and **4**' was accordingly denoted for such complex. Bulk crystals were collected for the record of <sup>1</sup>H NMR spectrum which supported the identity of **4**' with one ethyl

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Scheme 2. Synthesis of 1-4.

substituent of amino group converted into hydrogen, indicative of high degree of completeness for such conversion during recrystallization. It is noteworthy that oxidative N-dealkylation reactions have been observed in the presence of catalyst. Attempts have been made to verify the presence of possible catalyst in the form of impurity during the course of recrystallization, however no detectable candidate has been observed. The perspective drawings of complexes 1 and 4' are depicted in Figs. 1 and 2, respectively. The crystal structure determination data are listed in Table 1 and the selected bond lengths and angles are given in Table 2. To the best of my knowledge, they are the first examples showing the crystal structures of transition metal complex tethered with rhodamine derivative. For 1, the rhenium(I) metal centre coordinates to one rhodamine derivative tethered bipyridine chelate, three carbonyl ligands with facial arrangement, and one bromide groups to give a distorted octahedral geometry, characteristic of other rhenium(I) tricarbonyl diimine system [34–36]. The N(1)–Re(1)–N(2) bond angle of 74.5° about the rhenium(I) metal centre, deviated from the idealized values of 90°, is attributed to the bite distance exerted by the steric demand of the chelating bipyridine ligand. For 4', the coordination geometry at the iridium(III) metal centre was distorted octahedral with two cyclometalated dpgx and one rhodamine derivative-containing bipyridine (L1) lignads. The coordinated carbon atoms of two cyclometalated dpgx ligands are in a cis arrangement to each other and trans to the nitrogen atom of the bipyridine chelate. The Ir-C and Ir-N bond distances are normal and comparable to those in other related cyclometalated iridium(II) diimine system [37,38]. The Ir-N bond distances in the bipyridine chelate (2.17 and 2.19 Å) are longer than those in



**Fig. 1.** Perspective drawing of **1** with atomic numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 15% probability level.



**Fig. 2.** Perspective drawing of complex cation of complex **4**<sup>*t*</sup> with atomic numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 15% probability level.

the cyclometalated ligand (2.06 and 2.09 Å) because of the trans position of the cyclometalated carbon atom having stronger trans effect. It is interesting to note that the quinoxaline moiety and the cyclometalated phenyl ring are not co-planar with the interplanar angles of (25.8° and 19.9°), probably for the relief of the mutual repulsion. Similarly, the C-Ir-N (79.0° and 79.4°) and N-Ir-N (74.9°) bond angles about the iridium(III) metal centre were found to be less than 90°, as required by the bite distance exerted by the steric demand of the chelating cyclometalated and bipyridine ligands. In both 1 and 4', the molecular structure clearly indicates that the rhodamine derivatives are in ring-closed spirolactam form with the C-C-N bond angles (99.1° in 1 and 99.0° in 4') and N-C bond distances (1.51 Å in 1 and 1.53 Å in 4'). The C(15)-N(3)-N(4) bond angles (121.2° in 1 and 121.6° in 4′) and the C-N bond distances (1.29 Å in 1 and 1.27 Å in 4') about the imine group are typical of sp<sup>2</sup> C=N bond character. The co-planarity of the bipyridine ligand is extended through the C=N conjugation to the spirolactam group with the torsion angle of 178.3° and  $179.3^{\circ}$  in **1** [C(6)–C(15)–N(3)–N(4)] and **4**' [C(48)–C(52)–N(7)– N(8)], respectively.

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# $\begin{array}{l} \textbf{Table 2} \\ \textbf{S} elected \ bond \ lengths \ (\mathring{A}) \ and \ bond \ angles \ (deg) \ of \ 1 \ and \ 4'. \end{array}$

1		4′	
Bond lengths (Å)			
Re(1)-C(1)	1.93	Ir(1)-C(1)	1.99
Re(1)-C(2)	1.90	Ir(1)-C(21)	2.00
Re(1)-C(3)	2.00	Ir(1) - N(1)	2.06
Re(1)-N(1)	2.15	Ir(1)-N(3)	2.09
Re(1)-N(2)	2.17	Ir(1)-N(5)	2.19
Re(1)-Br(1)	3	Ir(1)-N(6)	2.17
C(1)-O(1)	1.13	C(52)–N(7)	1.27
C(2)-O(2)	1.18	N(7)-N(8)	1.34
C(3)-O(3)	0.95	N(8)-C(60)	1.53
C(15)-N(3)	1.29	C(59)-C(60)	1.51
N(3)-N(4)	1.35		
N(4)-C(23)	1.51		
C(22)-C(23)	1.53		
Bond angles (°)			
Re(1)-C(1)-O(1)	178.5	C(1)-Ir(1)-N(1)	79.4
Re(1)-C(2)-O(2)	177.2	C(21)-Ir(1)-N(3)	79.0
Re(1)-C(3)-O(3)	170.9	N(5) - Ir(1) - N(6)	74.9
N(1) - Re(1) - N(2)	74.5	C(52) - N(7) - N(8)	121.6
C(15)-N(3)-N(4)	121.2	N(8) - C(60) - C(59)	99.0
C(22) - C(23) - N(4)	99.1		

### 3.3. Photophysical behaviours

The electronic absorption behaviour of 1-4 has been studied in methanol at 298 K and the electronic absorption spectra are depicted in Fig. 3. The rhenium(I) complexes, 1 and 2, showed intense high-energy absorption bands at 275 and 318 nm with extinction coefficients of the order of 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, and a low-energy absorption band at about 380-400 nm. With reference to the spectroscopic features of other related rhenium(I) tricarbonyl diimine system [39,40], the high-energy absorption bands are assigned as  $\pi \to \pi^*$  transition of the bipyridine and rhodamine components, while the low-energy absorption band is ascribed to the  $[d\pi(\text{Re}) \rightarrow \pi^*(\text{bipy})]$  metal-to-ligand charge transfer (MLCT) transition. For the iridium(III) complexes, 3 and 4, a high-energy absorption band at 298 and 366 nm and a less intense low-energy absorption band at 472 nm were observed. The high-energy absorption bands are ascribed to  $\pi \rightarrow \pi^*$  transition of the 2,3-quinoxalinate, bipyridine and rhodamine moieties, whereas the low-energy absorption band is assigned as a spin-allowed metal-to-ligand charge transfer (MLCT)  $[d\pi(Ir) \rightarrow \pi^*(dpqx)]$  transition. Similar to the other related iridium(III) cyclometalated complexes [27,37,38], the observation of weak shoulder beyond 500 nm is probably due to the spin-forbidden <sup>3</sup>MLCT transition. The emission







Fig. 4. Normalized emission spectra of 3 and 4 in methanol at 298 K.

properties of complexes 1-4 have also been investigated and all of them were found to exhibit emission upon excitation at  $\lambda > 350$  nm in methanol at 298 K. Both complexes 1 and 2 are found to exhibit similar green emission at 565 nm. Such emission is probably attributed to the rhodamine B emission due to the presence of trace amount of the open form of rhodamine. Although the luminescence lifetime is of <0.1 µs, the assignment of emission origin derived from the <sup>3</sup>MLCT  $[d\pi(Re) \rightarrow \pi^*(bipy)]$  excited state could not be excluded. On the other hand, complexes 3 and 4 showed an intense emission band at 675 nm (Fig. 4). The large Stokes shifts and the observed luminescence lifetime of about 0.6 µs suggest that emission is from a triplet parentage. In view of the fact that a similar emission band at about 675 nm was observed in the rhodamine derivative-free model complex, [Ir(dpgx)<sub>2</sub>(4-carboxaldehyde-4'-methyl-2,2'-bipyridine)]PF6, such lower energy emission is ascribed to the triplet excited state of MLCT  $[d\pi(Ir) \rightarrow \pi^*(dpqx)]$ origin. Related iridium(III) 2,3-quinoxalinato complexes [27,37] have also been reported to show similar emission at about 622-670 nm with the assignment of <sup>3</sup>MLCT  $[d\pi(Ir) \rightarrow \pi^*(2,3-quinoxali$ nato)] excited state. It is interesting to note that a rather weak emission at 550 nm characteristic of rhodamine 6G in 3 was observed, probably due to the existence of trace amount of the open form of rhodamine 6G in methanol. No such rhodamine 6G emission was found in 4, suggesting that the introduction of ethylene group separating two nitrogen atoms may render the ring-closed form more stable in the same solvent system.

#### 3.4. Selective metal ion binding studies

Selective binding properties of complexes 1-4 have been investigated by electronic absorption and emission spectroscopic methods for various alkali, alkaline-earth and transition-metal cations, such as K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>. Solutions of **1**, **3** and **4** in methanol exhibit drastic colour changes from pale yellow to magenta selectively in the presence of Hg(II) ion, no observable colour was observed in **2** upon the addition of the same concentration of Hg(II) ion. Upon addition of Hg(II) ion, into the methanolic solution of 1, a new absorption band at 558 nm was observed in the electronic absorption spectra with increasing concentration of Hg(II) ion. The corresponding electronic absorption spectral changes are shown in Fig. 5(a). On the basis of the absorption band of rhodamine B occurred at similar energy, the emergence of such new absorption band is ascribed to the conversion of the spirolactam form to the corresponding ring-opened amide form upon Hg(II) ion binding in **1**. The  $\log K_s$  values for Hg(II) ion binding to **1** was found to be 4.76  $(\pm 0.12)$ , from the result of theoretical fit of the 1:1 stoichiometric

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**Fig. 5.** (a) The electronic absorption spectra of **1** in MeOH (concentration = 17.1  $\mu$ M) at 298 K upon addition of various concentrations of Hg<sup>2+</sup>. Inset shows the plots of the absorbance at 558 nm as a function of the concentration of Hg<sup>2+</sup>. (b) The emission spectra of **1** in MeOH (concentration = 17.1  $\mu$ M) at 298 K upon addition of various concentrations of Hg<sup>2+</sup>. Inset shows the plots of the emission intensity at 582 nm as a function of the concentration of Hg<sup>2+</sup>.

binding mode. On the other hand, no significant electronic absorption spectral changes were observed in **2**, indicative of its insensitivity for Hg(II) ion binding. Together with the amide group, the nitrogen atom on the imine unit is anticipated to involve in the coordination of Hg(II) ion. The poor sensitivity in **2**, as a result of the poor coordinating ability, is rendered by the separation of ethyl linker between amide moiety and imine nitrogen atom. is ascribed to the difference in the separation distance of the amide group from the nitrogen atom on the imine unit, which is anticipated to participate in the binding process of Hg(II) ion.

Similar emission titration experiments have also been performed to study the cation-sensing processes of complex **1**. Upon excitation at the isosbestic wavelength of 340 nm, the solution of **1** was found to exhibit a drastic emission enhancement at 588 nm with increasing the concentration of Hg(II) ion, attributed to the rhodamine B emission as a result of ring-opening process. The changes in emission intensities of **1** toward Hg(II) ion are featured in Fig. 5(b) and there is a red shift of the emission from 580 to 588 nm upon increasing the concentration of Hg(II) ion. Since the emission energies of the rhenium(I) tricarbonyl diimine system as well as the rhodamine B are very close, the mixing of the rhenium(I)-emission into such emission enhancement at 588 nm, as well as energy transfer between rhenium(I) complex and rhodamine B, is possible. Unlike to the absorption titration, no satisfac-



**Fig. 6.** (a) The emission spectral changes of **3** (a) and **4** (b) in methanol at 298 K upon addition of various concentrations of Hg(II) ion.

tory result could be obtained to find the binding constants of 1 for Hg(II) ion by the emission titration. The deviation from the theoretical binding fit probably due to the contribution of <sup>3</sup>MLCT emission from the rhenium(I) moiety at similar energy region. Similar to the electronic absorption study, no significant emission response was found in 2, showing the weak binding affinity and ring opening behaviour toward target Hg(II) ion. As reported in the previous communication [22], the corresponding electronic absorption and emission titrations of **3** and **4** have been studied. Both of them were found to exhibit ring opening process of the rhodamine derivative upon addition of Hg(II) ion into the methanolic solution. Their electronic absorption spectral changes are similar that there is a new absorption band at 530 nm and the absorbance was found to increase with the concentration of Hg(II) ion. The log  $K_s$  values for Hg(II) ion binding to **3** and **4** were found to be 4.55 ( $\pm 0.09$ ) and 3.63 ( $\pm 0.04$ ), respectively, from the result of theoretical fit of the 1:1 stoichiometric binding mode. The binding constants of complexes 1 and 3, which contain the almost same rhodamine appended diimine ligand, are comparable and in the same order of magnitude. It is interesting to note that 3 and 4 were found to show essentially different emission spectral changes upon Hg(II) ion binding. The iridium(III)-based MLCT emission intensity at 675 nm was found to increase greatly, with a slight increase in the rhodamine 6G emission at 555 nm, in 3, while only the rhodamine 6G emission was substantially enhanced with no observable change in the iridium(III) emission in 4 (Fig. 6). In the system of 3 as a bichromophoric array, the emission enhancement of iridium(III) luminophore is ascribed to an efficient intramolecular energy transfer process from rhodamine 6G to the cyclometalated iridium (III) moiety, upon the ring-opening of the rhodamine derivative. However, in the case of 4 with an ethyl group as non-conjugated linker between rhodamine 6G and the iridium(III) luminophore, such energy transfer is inefficient.

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## 4. Conclusion

A new class of transition metal complexes including rhenium(I) tricarbonyl diimine and cyclometalated iridium(III) diimine systems, which contain rhodamine derivative as a sensory moiety, have been synthesized and characterized. The X-ray crystal structures of 1 and 4' (4 with one ethyl substituent of amino group converted into hydrogen on the rhodamine derivative) have been determined. Their photophysical and selective ion-binding properties have also been investigated. 1 was found to exhibit selective binding toward Hg(II) ion with electronic absorption and emission spectral changes, while another rhenium(I) analogue, **2**, showed no such binding behaviour. Iridium(III) complexes, 3 and 4, were found to give similar electronic absorption response but different emission spectral changes upon addition of Hg(II) ion. Efficient intramolecular energy transfer from rhodamine 6G to the cyclometalated iridium (III) moiety was suggested in 3, which could be modulated by selective ion-binding process upon ring-opening of rhodamine 6G. Although comparable binding constants towards Hg(II) ion are obtained in **1** and **3** with almost the same rhodamine tethered diimine ligand, the variation of coordinating sphere of rhenium(I) or iridium(III) metal centre may also influence the binding affinities, probably due to the differences in the electronic effect and steric bulkiness, in particular to the cases of 2 and 4. This report shows that the modification of rhodamine derivatives and the choice of transition metal ion could be important to influence the selective binding properties for development of colorimetric and/or luminescent probe. Through a judicious design and choice of ligand systems with different functionalized bridging spacers, the selectivity of the sensing ability and the efficiency of energytransfer are anticipated to be varied.

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## Appendix A. Supplementary data

CCDC 986107 and 986108 contains the supplementary crystallographic data for **1** and **4**'. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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