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Colorimetric and luminescent bifunctional Ru(II) complexes for rapid and highly sensitive recognition of cyanide

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Four ruthenium(II) complexes, $[\text{Ru}(\text{bpy})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2\text{L2}](\text{PF}_6)_2$, $[\text{Ru}(\text{dmb})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$, where bpy = 2,2'-bipyridine, dmb = 4,4'-dimethyl-2,2'-bipyridine, L1 = 4-methyl-2,2'-bipyridine-4'-carboxaldehyde, L2 = 4,4'-diformyl-2,2'-bipyridine, have been characterized to sensing cyanide based on the well-known formation of cyanohydrins. The structure of $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ is also determined by single crystal X-ray diffraction. Their cyanide anion binding properties in pure and aqueous acetonitrile solution were thoroughly examined by UV-Vis absorption and photoluminescence (PL) spectroscopy. Upon the addition of cyanide to the solution of ruthenium(II) complexes at 298 K, a color change from orange to yellow and a luminescent variation from dark red to red-orange can be observed by the naked eye. The large blue-shift of the absorption and emission spectra and significant enhancement of the emission intensity upon the addition of cyanide could be attributed to the formation of a cyanohydrin group by selective reaction of the aldehyde group of ruthenium(II) complexes with cyanide. Importantly, this kind of ruthenium(II) complexes show an unique recognition of cyanide ions over other anions. The results reveal that this kind of ruthenium(II) complex containing aldehyde group is an eligible sensor for cyanide anion.

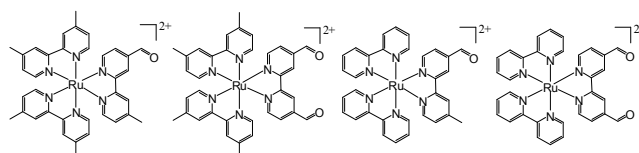
Introduction

Cyanide has a formidable toxicity¹ although it plays an important role in chemical industry² such as fibers, resins, herbicides, and the gold mining. The presence of cyanide has a great harm on the environment and human health³ because it can damage the body's central deep breath system and has a rapid onset process and acute poisoning characteristics. It can lead a serious consequence if we can not detect it and be treated timely.³ According to the World Health Organization, the maximum acceptable level of cyanide in drinking water is 1.9 μM .⁴ Due to the widespread application and highly toxic characteristics of cyanide, development of new probes for high selective and qualitative detection of cyanide ions is of great importance.⁵ Various colorimetric and fluorometric methods⁶ were developed for the sensing of cyanide ions, in which many transition metal complexes involved element such as Zn,^{6c} Ir,^{5c,d} Co^{5e} and Ru⁷ have been designed as cyanide receptors. But the most of it have to face with the problem of slow reaction rate,^{6a,b} special requirements,^{6c,d} poor selectivity regarding for fluoride and acetate^{6b,e,f} as interfering anions. Recently, the reaction-based sensors^{8,9} or chemodosimeters has attracted considerable interest.¹⁰ The various probes for cyanide ion sensing such as quantum dots,¹¹ polymeric materials,¹² nanoparticles¹³ and radical anion¹⁴ have been investigated.

Ruthenium(II) polypyridyl complexes are attractive for development of luminescent sensors,^{7,15} photoinduced switches,¹⁶ dye-sensitized solar cells (DSSC),¹⁷ especially in chemosensors or probes¹⁸ due to their rich photophysical and photochemical properties such as visible excitation wavelengths, large Stoke

shifts, relatively long excited state lifetimes, high stability in aqueous media compared with those of pure organic luminophores. Although there are a number of reports about chromogenic and luminescent receptors/probes based on ruthenium(II) polypyridine complexes for the selective and sensitive sensing of metal ions,¹⁹ anions,²⁰ molecular oxygen²¹ and biologically relevant molecules²² in recent years, there are only several reports for the selective and sensitive recognition of the cyanide anion,²³ and the methods of direct detection of cyanide are usually hampered by interference from molecules such as acetate and fluoride. Consequently, further development of a selective luminescent probe for CN⁻ sensor in analytical- and bio-systems is still a challenge.

In the present study, a series of ruthenium(II) complexes, $[\text{Ru}(\text{dmb})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2\text{L2}](\text{PF}_6)_2$, where bpy = 2,2'-bipyridine, dmb = 4,4'-dimethyl-2,2'-bipyridine, L1 = 4-methyl-2,2'-bipyridine-4'-carboxaldehyde, L2 = 4,4'-diformyl-2,2'-bipyridine, functionalized with electron-deficient carbonyl units (Scheme 1), were characterized and used for sensing of cyanide ions. This carbonyl group is expected to reduce the interference of acetate and fluoride because the cyanide ion (CN⁻) has a particularly strong affinity to C=O.^{10a,b,c,24} Their interaction with cyanide was investigated by UV-Vis absorption, photoluminescence (PL) and ¹HNMR spectroscopy. The complexes were found to show colorimetric and luminescent bi-function toward cyanide ions.



[Ru(dmb)₂L1]²⁺ [Ru(dmb)₂L2]²⁺ [Ru(bpy)₂L1]²⁺ [Ru(bpy)₂L2]²⁺
Scheme 1 Chemical structures of the ruthenium(II) complexes.

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Experimental Section

Materials

Four ruthenium(II) complexes $[\text{Ru}(\text{dmb})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2\text{L1}](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2\text{L2}](\text{PF}_6)_2$ were prepared according to literature methods.^{22c} The salt KCN, NaCl, NaNO₃, Na₂CO₃, NaAcO, NaF, NaH₂PO₄, Na₂SO₄, NaN₃ and NaHCO₃ were purchased from Sinopharm Chemical Reagent Co. Ltd. High performance liquid acetonitrile was purchased from Sinopharm Chemical Reagent Co. Ltd. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) were purchased from Alfa Aesar China (Tianjin) Co. Ltd., which was recrystallized from hot ethanol and dried in vacuo at 110 °C before use. All chemicals were analytical reagent grade and used as received.

Methods and instrumentations

¹H NMR spectra were measured on a BRUKER 400MHz Digital NMR Spectrometer. Chemical shifts (ppm) were reported relative to tetramethylsilane (Me₄Si). Positive-ion electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo Finnigan LCQ Deca XP mass spectrometer (Finnigan, USA). UV-Vis absorption spectra were taken on TU-1950 UV model spectrophotometer. Emission spectra were carried out by a LS-55 spectrophotometer (Perkin Elemer).

Crystal structural determination

Crystal data for $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$: $[\text{C}_{36}\text{H}_{32}\text{F}_{12}\text{N}_6\text{O}_2\text{P}_2\text{Ru}]$, fw=971.69, trigonal, R-3c, $a = b = 31.553(3)$ Å, $c = 25.580(5)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 22055(5)$ Å³, $Z = 18$, $D_c = 1.317$ g.cm⁻³, $\mu = 0.465$ mm⁻¹, $F(000) = 8784$ and $T = 194(2)$ K. The crystallographic data collection was carried out on a beam line 3W1A at BSRF (Beijing Synchrotron Radiation Facility) with a mounted MarCCD-165 detector using synchrotron radiation ($\lambda = 0.8000$ Å) at $T = 194$ K. Data reduction and numerical absorption correction were applied with HKL2000 software.²⁵ The structure was solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXH-97 crystallographic software package.²⁶ The hydrogen atoms of the complex were generated geometrically with isotropic thermal parameters. A total of 12301 reflections were measured, including 2508 unique ($R_{\text{int}} = 0.0627$) reflections of which 1897 [$I > 2\sigma(I)$] reflections were used for refinement with $R1 = 0.0775$ and $wR2 = 0.2472$ with a goodness of fit of 1.103.

Results and discussion

Crystal structure

Single crystals of $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ were obtained by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The perspective drawing of the complex cation is shown in Fig. 1. The Ru(II) ion is coordinated by two ancillary 4,4'-dimethyl-bipyridines and one L2 ligand in a distorted octahedral geometry (Fig. 1). The angle subtended by the N atoms of 4,4'-dimethyl-bipyridine and L2 ligand at the Ru center is

78.4(4)° and 78.5(3)°, respectively, which is much smaller than the ideal angle of 90° adopted in the octahedral geometry. This deviation from the ideal angle due to the steric requirement of the chelating ligands was commonly observed in other related complex systems.^{21a,27} The bond distances of Ru(1)-N(1), Ru(1)-N(2) and Ru(1)-N(3) are 2.052(6), 2.052(8) and 2.050(8) Å, respectively, which were typical of those found in other ruthenium(II) polypyridyl complexes.^{27,28} The bond distance of C(18)-O(1) is 1.222(16) Å, which is similar to typical carbonyl bond length (C=O 1.22 Å).

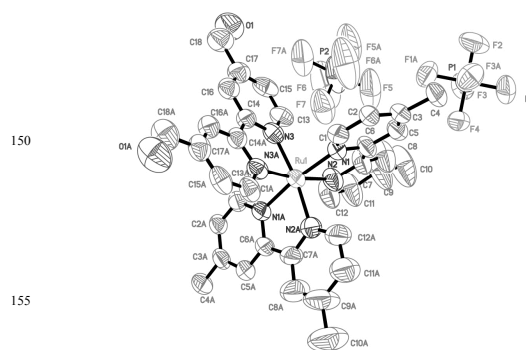


Fig. 1 ORTEP drawing of $[\text{Ru}(\text{dmb})_2\text{L2}]^{2+}$ with atom labelling scheme showing 30% thermal ellipsoids.

Photophysical properties

The electronic absorption (20 μM) and photoluminescence (PL) spectra of four complexes (5 μM) in CH₃CN/H₂O (99.6:0.4 v/v) solution under ambient condition are shown in Fig. 2. All of the ruthenium(II) complexes show typical MLCT (metal to ligand charge transfer) absorption bands between 380 and 550 nm, while the intense absorption band at about 285 nm is attributed to intraligand (IL) $\pi-\pi^*$ transitions, similar to that observed in other related ruthenium(II) complex systems.^{20d,21a,29} The complexes containing L2 ligand, $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2\text{L2}](\text{PF}_6)_2$, show two distinguishable bands in the MLCT transitions. The lower energy MLCT band at about ca. 485-505 nm is ascribed to a metal ($d\pi(\text{Ru})$) to L2 ligand (π^*) charge transfer since the electron withdrawing character of the two CHO groups and their π conjugation with the bipyridine should efficiently decrease the LUMO (π^*) energy. The higher energy band at about 425 nm is attributed to a metal ($d\pi(\text{Ru})$) to ancillary 2,2'-dipyridyl/4,4'-dimethyl-2,2'-dipyridyl ligand. The complexes were found to show weak emission (Fig. 2) at ca. 705-745 nm at room temperature upon excitation at $\lambda < 500$ nm, assigned as derived from a ³MLCT excited state, which is typical of related ruthenium(II) complexes.^{15a,20d,21a} The weak emission of the Ru(II) complexes could be explained by the strong electron-withdrawing property of the aldehyde group in the ligand that stabilize the π^* orbital and decrease the energy gap between the ligand π^* and $d\pi(\text{Ru})$ orbitals, then the non-radiative transition increase and the MLCT luminescence efficiency of the complexes would decrease. The strong electron-withdrawing property of two aldehyde groups in L2 also resulted in a small red

shift of emission maxima for the complexes containing L2
190 compared to L1.

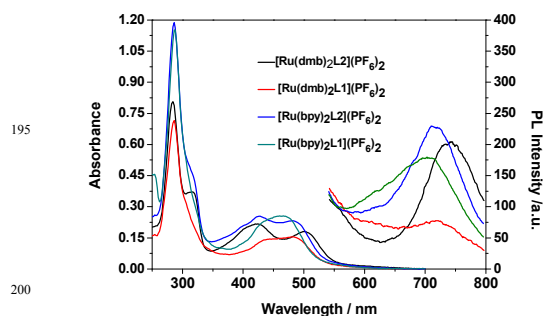


Fig. 2 UV-Vis (left) and PL (right) spectra of four ruthenium(II) complexes in CH₃CN/H₂O (99.6:0.4 v/v) solution at room temperature.

Cyanide anion sensing studies

a. Electronic absorption spectroscopy

Firstly, the recognition of CN⁻ by the complexes was studied by using a spectrophotometric absorption method. Spectral changes
210 in the both IL transition bands and MLCT bands were observed upon the addition of cyanide ions to the acetonitrile–aqueous (99.6:0.4 v/v) solution of the ruthenium(II) complexes containing 50mM Bu₄NPF₆. Upon the addition of CN⁻ to [Ru(dmb)₂L1](PF₆)₂ with one aldehyde group, the absorption intensity at ca. 485 nm decreased and the absorption intensity at ca. 459 nm increased slightly with a blue shift of about 26 nm and a well-defined isosbestic point at 475 nm in the MLCT band. The similar spectral changes were obtained for [Ru(bpy)₂L1](PF₆)₂ under the same conditions after the addition of CN⁻ (Fig. S1, Supporting
220 information). While upon addition of CN⁻ to the CH₃CN/H₂O (99.6:0.4 v/v) solution of [Ru(dmb)₂L2](PF₆)₂ (20 μM) containing 50mM Bu₄NPF₆, there were significant changes in the UV-vis spectra, especially in the MLCT bands (Fig. 3(a)). A gradual decrease of the absorbance at 422 and 505 nm and a new absorption band at 460 nm were observed upon the addition of
225 CN⁻ to [Ru(dmb)₂L2](PF₆)₂ at room temperature as shown in Fig. 3(a). Two isosbestic points at ca. 435 and 485 nm can be observed in the MLCT region during the course of the UV-Vis absorption titration. Some changes in the LC region were also observed. With the blue shift of MLCT band from 505 nm to 460 nm (Δλ ≈ 45 nm), a prominent color change from orange to yellow could be readily observed by the naked eye upon addition of cyanide ions to the complex solutions as shown in inset of Fig. 3(b). All these phenomena indicate that new substances were formed. A plot of the absorbance at λ₄₆₀ nm as a function of the amount of cyanide was shown in inset of Fig. 3(a). The absorbance was increased upon the addition of CN⁻, and reached saturation at about 5.5 equiv of CN⁻. The similar phenomena were observed for [Ru(bpy)₂L2](PF₆)₂ upon the addition of CN⁻ (Fig. S1). Compared
240 to [Ru(bpy)₂L1](PF₆)₂ and [Ru(bpy)₂L2](PF₆)₂, the absorbance was increased gradually in the trace of CN⁻ (0 ~2 equiv) and the changes become more drastic and rapid over 2 equiv before it reached saturation for [Ru(dmb)₂L1](PF₆)₂ and

[Ru(dmb)₂L2](PF₆)₂. The results show that the electron-donating
245 groups such as -CH₃ would decrease the kinetic reactivity. This phenomenon was also observed in the previous reports³⁰ and stronger electron-withdrawing groups were advised to establish higher kinetic reactivity and equilibrium constants.

250 From the above result, it is evident that the existence of CN⁻ significantly affects the photophysical properties of ruthenium(II) complexes with electron-withdrawing groups (-CHO). A much less electron-withdrawing character of the cyanohydrin groups would generate after the addition of cyanide to the Ru(II) complexes functionalized with -CHO group (Scheme 2), which apparently shorten its conjugated chain length and significantly enhance the LUMO (π*) energy level. Partial or full MLCT would switch from dπ(Ru) → L1 /L2(π*) to dπ(Ru) → bpy/dmb(π*) after reaction with cyanide. All these resulted in a large blue shift of MLCT absorption peak. In addition, the disappearance of the intraligand n → π* transition at ca. 315 nm in the LC field could be explained by the fact that the carbonyl group (C=O) in complexes would no longer be available after reaction with cyanide ions. The studies also showed that more aldehyde groups in the ruthenium(II) complexes would cause larger spectral changes in the UV-vis spectra upon addition of CN⁻, indicating that aldehyde groups definitely play a key role in the recognition of cyanide ions.

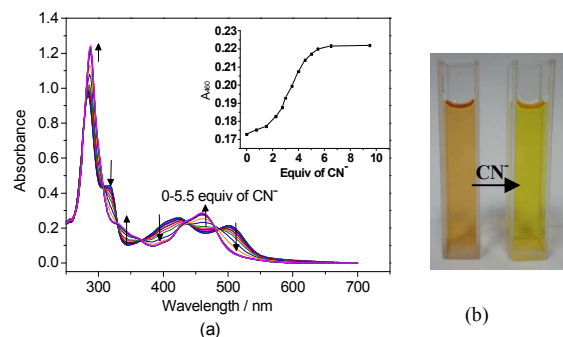
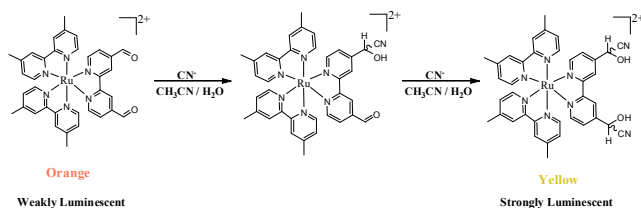


Fig. 3 (a) UV-Vis absorption titration of [Ru(dmb)₂L2](PF₆)₂ (20μM) with CN⁻ solution (0–5.5 equiv) in CH₃CN/H₂O (99.6:0.4 v/v) containing 50mM Bu₄NPF₆ at 25 °C; The inset shows plot of A₄₆₀ against the amount of added CN⁻; (b) Photograph shows the color change from orange red to yellow upon addition of CN⁻ to
275 [Ru(dmb)₂L2](PF₆)₂ solution.



Scheme 2 Cyanide detection by probe [Ru(dmb)₂L2](PF₆)₂ based on cyanohydrins' formation.

b. Photoluminescent properties

The ability of ruthenium(II) complexes to sensing cyanide ions was also investigated using a photoluminescent method. The emission spectra of the ruthenium(II) complexes show a pronounced changes after CN^- ions was added. The luminescence spectra of $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ complexes upon treatment with CN^- are shown in Fig. 4(a). Complex $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ (5.0 μM) shows a rather poor emission at about 745 nm upon excitation at 485 nm ($\lambda_{\text{exc}} = 485 \text{ nm}$, isosbestic point of UV-vis titration). The disappearance of emission at 745 nm and a new gradual appearance of the PL band at ca. 618 nm were observed with increasing amounts of CN^- ions. The emission color gradually changed from dark red to red-orange as shown in Fig. 4(b). The emission maximum shows a notable blue shift ($\Delta\lambda \approx 127 \text{ nm}$) and the spectral change is negligible when more than 5.5 equiv CN^- is added. The emission intensity at ca. 618 nm was significantly enhanced by about 17-fold. The plot of the PL intensity change ($I - I_0$) at 618 nm for $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ as a function of the cyanide concentration was shown in the inset of Fig. 4(a), which is comparable to that of its UV-Vis titration. Interestingly, studies of the luminescent properties of all the other three ruthenium(II) complexes in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) solutions containing 50 mM Bu_4NPF_6 show that only the addition of cyanide induced a large enhancement of the phosphorescent emission intensity at about $\lambda_{618 \text{ nm}}$ (Fig. S2, Supporting information), corresponding to an obvious variation in emission color from dark red to orange-red. And the blue shift of the emission maximum for $[\text{Ru}(\text{dmb})_2\text{L1}](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2\text{L2}](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2\text{L1}](\text{PF}_6)_2$, is about 102, 97 and 90 nm, respectively. The significant enhancement of the emission intensity and the large blue shift of the emission maxima are ascribed to the reaction of aldehyde group of the complex with cyanide ions, similar changes were observed in the related complex.^{15a} The results also demonstrated that more aldehyde groups and substitution with electron-donating group (CH_3) on the bpy in the complexes would cause larger spectral changes in the emission spectra after addition of cyanide ions. These results were in agreement with the observed trends in the studies using the UV-vis spectrophotometric method..

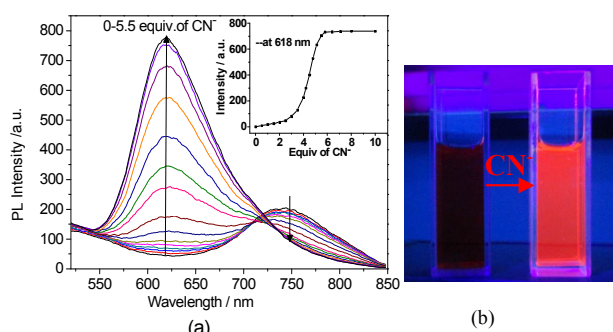


Fig. 4 (a) PL titration of $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ (5 μM) with CN^- solution (0–10 equiv) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) containing 50 mM Bu_4NPF_6 at 25 °C; The inset shows plot of the PL intensity change ($I - I_0$) at $\lambda_{618 \text{ nm}}$ upon addition of CN^- . (b) Photograph shows the orange luminescence after addition of CN^- to $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$.

c. Reaction of the ruthenium(II) complexes with cyanide

The reaction of the ruthenium(II) complexes with cyanide was also confirmed by positive-ion ESI-MS experiments. The 1:1 adduct, $\{[\text{Ru}(\text{bpy})_2(\text{L1-CN})]^{2+}\text{CN}^-\}^+$ and the 1:2 adduct, $\{[\text{Ru}(\text{dmb})_2(\text{L2-2CN})]^{2+}\text{PF}_6^-\}^+$ were observed as ion clusters at m/z , 664.3 and 880.7, respectively, in the positive-ion ESI-mass spectrum of an acetonitrile solution of $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$ or $[\text{Ru}(\text{dmb})_2(\text{L2})](\text{PF}_6)_2$ and CN^- . The ESI-mass spectra are listed in the supporting information Fig. S6. A small signal for the 1:1 adduct, $\{[\text{Ru}(\text{dmb})_2(\text{L2-CN})]^{2+}\text{CN}^-\}^+$ was also observed as ion cluster at m/z 735.2, which shows it is a stepwise process in the reaction. The results demonstrated that all aldehyde groups in the complexes would react with CN^- . ^1H NMR spectroscopy of $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$ after addition of CN^- in CD_3CN was also carried out to confirm the reaction of the ruthenium(II) complexes with CN^- . Upon the addition of CN^- , the signal at ca. 10.2 ppm corresponding to CHO was weakened, and the new signal corresponding to cyanohydrin $-\text{CHCN}(\text{OH})$ appeared at ca. between 4–5 ppm as shown in (Supporting information Fig. S7). For $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$, the signal at ca. 9.0 ppm was also weakened, and a broad signal at ca. 9.7 ppm appeared. The results further demonstrated that CN^- could conjugate with the aldehyde group of the ruthenium(II) complexes.

Compared to the related Ru(II) complexes containing 1,10-phenanthroline-4,7-dicarboxaldehyde ligand,^{7a} the larger blue shifts in the UV-vis and luminescent spectra were observed after addition of CN^- in our systems. The results also show that the electron-donating groups such as $-\text{CH}_3$ would decrease the kinetic reactivity, and the stronger electron-withdrawing groups were expected to be favourable to the higher kinetic reactivity and equilibrium constants.

360 Selectivity and sensitivity

High selectivity is necessary for an excellent chemosensor. The investigation of the selective response of ruthenium(II) complexes was performed by UV-Vis and PL spectra when other anions was added. As stated the above, the ruthenium(II) complexes containing $-\text{CHO}$ group can selectively react with cyanide, resulting in a notable change of color by naked eyes, an apparent blue-shift in the absorption and emission spectra and an increase in emission intensity. In contrast, no remarkable change was observed by neither naked colors nor in UV-vis, PL spectra upon addition of other possibly competing anions (Cl^- , NO_3^- , CO_3^{2-} , F^- , H_2PO_4^- , SO_4^{2-} , HCO_3^- and NaN_3 , 5.5 equiv) to the solution of $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) solution containing 50 mM Bu_4NPF_6 in the absence of cyanide (Fig. 5). There were also no obvious effect on the enhancement of the emission intensity when an excess of other anions (55 equiv) was added to $[\text{Ru}(\text{dmb})_2\text{L2}](\text{PF}_6)_2$ in the presence of 5.5 equiv of CN^- (Fig. 6), indicating that the phenomenon was reproducible. The emission intensity of the complex was enhanced by about 2-fold and 3-fold after addition of 5.5 and 55 equiv of AcO^- , respectively. While a much more significant enhancement (16-fold) in the emission intensity of the complex was observed in the presence of 1.0 equiv of CN^- . No obvious changes were observed in color and UV-vis spectra after addition of AcO^- (5.5 and 55 equiv), although

there was a small enhancement in the emission intensity. Therefore, $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ may be considered as a highly selective probe for CN^- . The test of three other ruthenium(II) complexes also show that the ruthenium complexes may be considered as a highly selective probe for CN^- . (Fig. S4, Supporting information).

Moreover, $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ shows a high sensitivity toward CN^- due to the significant enhancement in PL intensity in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v). To further understand the sensibility of the ruthenium(II) complexes toward the cyanide, the time course of the PL response of $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ upon addition of 5.5 equiv of cyanide in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) containing 50 mM Bu_4NPF_6 at room temperature was monitored. The results show that the full response was fast and needs about 3.6 minutes. The response time of three other ruthenium(II) complexes was about 2-4 mins (Supporting information Fig. S5).

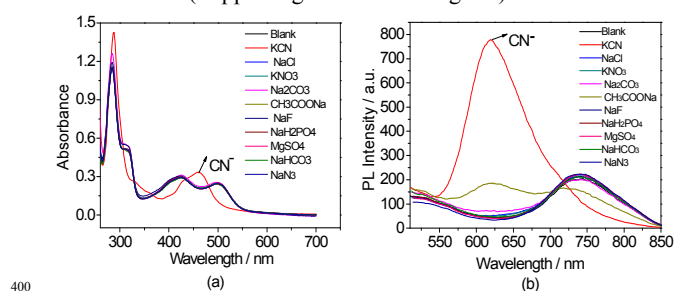


Fig. 5 (a) UV-Vis absorption spectra of $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ (20 μM) with different anions (5.5 equiv) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) containing 50 mM Bu_4NPF_6 . (b) PL spectra of $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ (5 μM) with different anions (5.5 equiv) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) containing 50 mM Bu_4NPF_6 .

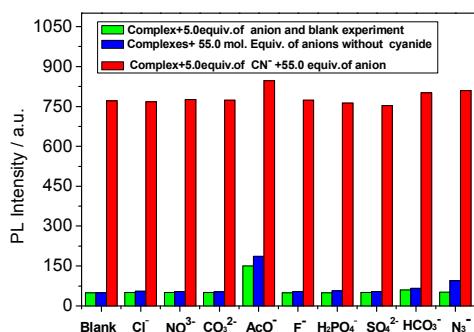


Fig. 6 Behavior of $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ toward CN^- and other anions as measured by PL in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) containing 50 mM Bu_4NPF_6 .

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Detection of CN^- in aqueous solution

PL titrations were carried out in different acetonitrile aqueous solution. $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ is weakly emissive at 745 nm upon excitation at 485 nm (isosbestic point of the UV-Vis titration) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v). A gradual enhancement of the intensity at 618 nm and the disappearance of weak emission peak

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at 745 nm were observed with increasing amounts of CN^- in PL titration. The emission at 745 nm underwent a small blue shift when the ratio of the water in acetonitrile solution (1 %, 3.0 %, 5.0 %) increased (Fig. 7). Especially for 50.0 % H_2O , the emission peak shifted to 645 nm (Fig. 7) due to the high polarity of the solvent. After addition of CN^- , the new emission peak at about 618 nm underwent a red shift. The emission maxima are about 620, 630, 635 and 650 nm for 1 %, 3.0 %, 5.0 % and 50.0 % water, respectively. The amount of CN^- and the response time (Fig. 8) for the saturation of the emission enhancement also increased with increasing the ratio of the water. The amount of CN^- is 6.5, 8.0, 10.0 equivalent, and the response time is 5.0, 7.0, 11.0 minutes for 1 %, 3.0 % and 5.0 % water, respectively. It is difficult to get the accurate amount of CN^- and response time for the saturation of the emission enhancement in 50% water. The results imply a gradual slower reaction as the water increases. This result is consistent with previously report, where the strong hydration of CN^- in aqueous solution would reduce its nucleophilicity^{24c}. In conclusion, $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (99.6:0.4 v/v) solution is the most suitable for high sensitive detection of CN^- , and this method is fast and sensitive.

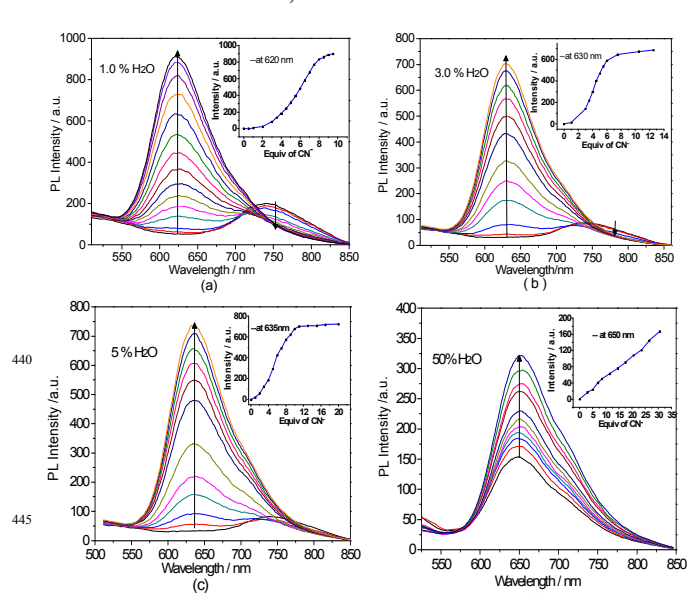
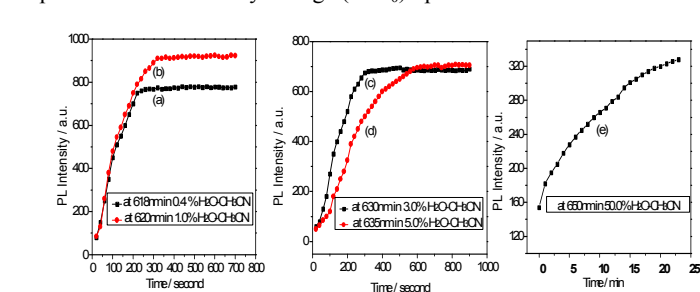


Fig. 7 Behavior of $[\text{Ru}(\text{dmb})_2\text{L}_2](\text{PF}_6)_2$ toward CN^- as measured by PL in aqueous acetonitrile containing 50 mM Bu_4NPF_6 at 25 $^{\circ}\text{C}$ (a) 1 % H_2O ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 99.0:1.0 v/v). (b) 3 % H_2O ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 97.0:3.0 v/v). (c) 5 % H_2O ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 95:5.0 v/v) (d) 50% H_2O ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 50.0:50.0 v/v). The inset shows plot of the PL intensity change ($I - I_0$) upon addition of CN^- .



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Fig. 8 Time course of the photoluminescence response of [Ru(dmb)₂L2](PF₆)₂ upon addition of CN⁻ in aqueous acetonitrile containing 50 mM Bu₄NPF₆ at 25 °C (a) 0.4 % H₂O (CH₃CN/H₂O, 99.6:0.4 v/v). (b) 1 % H₂O (CH₃CN/H₂O, 99.0:1.0 v/v). (c) 3 % H₂O (CH₃CN/H₂O, 97.0:3.0 v/v). (d) 5.0 % H₂O (CH₃CN/H₂O, 95.0:5.0 v/v). (e) 50% H₂O (CH₃CN/H₂O, 50.0:50.0 v/v).

Conclusion

In conclusion, a highly selective and sensitive chemosensor for cyanide based on the phosphorescent ruthenium(II) complexes functionalized with aldehyde group was presented. In particular, the complex shows a color change by the naked eye which provides a simple real-time method for cyanide detection. As the reaction between CN⁻ and the aldehyde groups of the complexes happens, a cyanohydrin forms which resulting in a partial MLCT switching. The results also show that the electron-donating groups such as -CH₃ would decrease the kinetic reactivity. This understanding of the CN⁻ sensing mechanism should help in the design of new phosphorescent probes based on ruthenium (II) complexes by the simple modification of the chemical structure of ligands to contain specific coordinating elements and in the exploration of new applications for cyanide chemosensors.

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Supporting information available

The UV-Vis and PL spectra of other three Ru(II) complexes after addition of cyanide ions. PL spectra of other three Ru(II) complexes (5 μM) with different anions. Time course of the photoluminescence response of other three Ru(II) complexes upon addition of CN⁻. ESI-MS spectra of the 1:1 {[Ru(bpy)₂(L1-CN)]²⁺CN⁻}⁺, 1:1 {[Ru(dmb)₂(L2-CN)]²⁺CN⁻}⁺ and the 1:2 adduct, {[Ru(dmb)₂(L2-2CN)]²⁺PF₆⁻}⁺, ¹H NMR spectroscopy of [Ru(bpy)₂(L1)](PF₆)₂ after addition of CN⁻, and X-ray crystallographic data in CIF format.

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Table of Contents

Four novel ruthenium(II) complexes have been characterized for colorimetric and luminescent bi-functional sensing of cyanide ions. The structure of one complex is also determined by single crystal X-ray diffraction. A color change from orange to yellow and a luminescent variation from dark red to red-orange can be observed by the naked eye upon the addition of cyanide to the solution of ruthenium(II) complexes.

