Organometallics **2006,** *25,* 3537−3540

Selective Luminescence Chemosensing of Potassium Ions Based on a Novel Platinum(II) Alkynylcalix[4]crown-5 Complex

Hiu-Suet Lo, Sung-Kong Yip, Keith Man-Chung Wong, Nianyong Zhu, and
Vivian Wing-Wah Yam*

*Center for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research,
Department of Chemistry and Open Laboratory of Chemical Biology of the
Institute of Molecular Technology for Drug Discovery and Synthesis,
The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China*

Received March 7, 2006

Summary: A novel dinuclear platinum(II) alkynylcalix[4]crown-5 complex has been demonstrated to show luminescence enhancement upon metal ion-binding, with a more selective binding toward K^+ over the other alkali-metal and alkaline-earth-metal ions.

Calixarenes and calixcrowns represent an important class of macrocyclic hosts, and they have been studied extensively in the past decade, owing to their unique molecular structures with tunable molecular shapes and conformations, their ease of undergoing chemical transformations, and their well-known supramolecular host-guest chemistry.[1] Incorporation of chromophoric and/or luminophoric moieties has also been shown to afford optical addressable selective molecular recognition probes.[2] Despite growing interest in this area, most of the works involved the employment of organic chromophores/luminophores, with transition-metal complex systems being less extensively explored,[3−5] in particular those other than d^6 metal complex chromophores.[4,5] Recently, we reported the synthesis and photophysical properties of a series of di- and tetranuclear gold(I) alkynylcalixcrown complexes[4] and showed that the incorporation of transition-metal centers in the calixarene framework might significantly perturb the shape or the structural properties of the calixarene unit. It has also been thought that a combination of the intrinsic properties typical of both the transition-metal centers and the calixcrown might lead to exploitation of such complexes in molecular recognition and chemosensing work.[3g−i,4,5] While there have been studies on d^6 metal-containing calixarene complexes that functioned as receptors,[3] studies based on other metal complex systems[4,5] are scarce, and reports on calixarene- or calixcrown-containing transition-metal complex systems that were capable of functioning as luminescence metal-cation probes have been relatively less explored.[3d,e,4] Despite increasing interest in the investigation of the richly luminescent platinum terpyridyl complexes in recent years,[6,7] due to the intriguing polymorphism in the solid states, solvent-induced aggregation, and interesting spectroscopic and luminescence properties that resulted from the presence of metal−metal interactions and $\pi-\pi$ stacking of the polypyridyl ligands,[6−8] exploitation of these systems in chemosensing work has been relatively less intense. As an extension of our previous

---

* To whom correspondence should be addressed. E-mail: wwyam@hku.hk. Fax: +(852) 2857−1586. Tel: +(852) 2859-2153.

[1] (a) Gutsche, C. D. *Calixarenes: Monographs in Supramolcular Chemistry*; The Royal Society of Chemistry: Cambridge, U.K., 1989. (b) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, U.K., 1998. (c) Asfari, Z. *Calixarenes 2001*; Kluwer Academic: Dordrecht, The Netherlands, 2001. (d) Gutsche, C. D.; Iqbal, M. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. 8, p 75. (e) Shinkai, S. *Tetrahedron* **1993**, *49*, 8933. (f) Böhmer, V. *Angew. Chem.* **1995**, *107*, 785; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.

[2] (a) Vogler, A.; Adamson, A. W. *J. Am. Chem. Soc.* **1968**, *90*, 5943. (b) Jang, Y. J.; Jun, E.; Lee, J. Y.; Kim, Y. S.; Kim, J. S.; Yoon, J. *J. Org. Chem.* **2005**, *70*, 9603. (c) Kim, S. K.; Lee , S. H.; Lee, J. Y.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499. (d) Ji, H. F.; Dabestani, R.; Brown, G. M.; Sachleben, R. A. *Chem. Commun.* **2000**, *10*, 833. (e) Nabeshima, T.; Saiki, T.;. Iwabuchi, J.; Akine, S. *J. Am. Chem. Soc.* **2005**, *70*, 1704. (f) Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S. K.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 2348. (g) Malval, J. P.; Leray, I.; Valeur, B. *New J. Chem.* **2005**, *29*, 1089.

[3] (a) Szemes, F.; Hesek, D.; Chem, Z.; Dent, A. W.; Drew, M. G. B.; Goulden, A. J.; Graydon, A. R.; Grieve, A.; Mortimer, R. J.; Wear, T.; Weightman, J. S.; Beer, P. D. *Inorg. Chem.* **1996**, *35*, 5868. (b) Beer, P. D. *J. Chem. Soc., Chem. Commun*. **1996**, 689. (c) Beer, P. D.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V. *Chem. Commun.* **1999**, 1755. (d) Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *Dalton Trans.* **2001**, *4*, 392. (e) Beer, P. D.; Szemes, F.; Passaniti, P.; Maestri, M. *Inorg. Chem.* **2004**, *43*, 3965. (f) Beer, P. D.; Cooper, J. B. *Chem. Commun.* **1998**, 129. (g) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645. (h) Cram, D. J.; Lein, G. M. *J. Am. Chem. Soc.* **1985**, *107*, 3657. (i) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc.* **1989**, *111*, 7567.

[4] (a) Yip, S. K.; Cheng, E. C. C.; Yuan, L. H.; Zhu, N.; Yam, V. W. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4954. (b) Yam, V. W. W.; Yip, S. K.; Yuan, L. H.; Cheung, K. L.; Zhu, N.; Cheung, K. K. *Organometallics* **2003**, *22*, 2630. (c) Yam, V. W. W.; Cheung, K. L.; Yuan, L. H.; Wong, K. M. C.; Cheung, K. K. *Chem. Commun.* **2000**, 1513.

[5] (a) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1995**, *34*, 323. (b) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, 145. (c) Vezina, M.; Gagnon, J.; Villeneuve, K.; Drown, M.; Harvey, P. D. *Chem. Commun.* **2000**, 1073. (d) Vezina, M.; Gagnon, J.; Villeneuve, K.; Brown, M.; Harvey, P. D. *Organometallics* **2001**, *20*, 273.

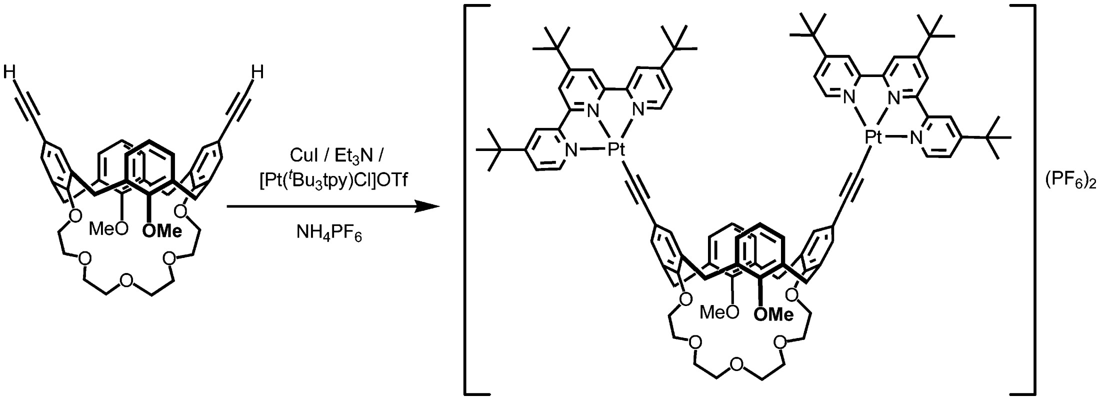
[6] (a) Jennette, K. W.; Gill, J. T.; Sadownick, J. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6159. (b) McMillin, D. R.; Moore, J. J. *Coord. Chem. Rev.* **2002**, *229*, 113. (c) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schacfer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591. (d) Büchner, R.; Cunningham, C. T.; Field, J. S.; Haines, R. J.; McMillin, D. R.; Summerton, G. C. *J. Chem. Soc., Dalton Trans.* **1999**, 711. (e) Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Ko, C. C.; Cheung, K. K. *Inorg. Chem.* **2001**, *40*, 571. (f) Yip, H. K.; Che, C.-M.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369. (g) Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1993**, *32*, 369. (h) Hill, M. G.; Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 4585.

[7] (a) Tang, W. S.; Lu, X. X.; Wong, K. M. C.; Yam, V. W. W. *J. Mater. Chem.* **2005**, *15*, 2714. (b) Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 4476. (c) Wong, K. M. C.; Tang, W. S.; Lu, X. X.; Zhu, N.; Yam, V. W. W. *Inorg. Chem.* **2005**, *44*, 1492. (d) Wong, K. M. C.; Tang, W. S.; Chu, B. W. K.; Zhu, N.; Yam, V. W. W. *Organometallics* **2004**, *23*, 3459. (e) Yam, V. W. W.; Wong, K. M. C.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 6506. (f) Yam, V. W. W.; Wong, K. M. C.; Zhu, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1400. (g) Yang, Q. Z.; Wu, L. Z.; Wu, Z. X.; Zhang, L. P.; Tung, C. H. *Inorg. Chem.* **2002**, *41*, 5653.

[8] (a) Houlding, V. H.; Miskowski, V. M. *Coord. Chem. Rev.* **1991**, *111*, 145. (b) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1989**, *28*, 1529. (c) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446. (d) Miskowski, V. M.; Houlding, V. H.; Che, C. M.; Wang, Y. *Inorg. Chem.* **1993**, *32*, 2518.

10.1021/om060218f CCC: $33.50

Scheme 1. Synthetic Route for Complex 1



works on the gold(I) alkynylcalixcrown systems,[4] together with the intriguing spectroscopic and photophysical properties of platinum(II) terpyridyl complexes and our recent demonstration of utilizing alkynylplatinum(II) terpyridyl crown ether-containing complexes as colorimetric and luminescence probes,[7a,b] we report herein the synthesis of a dinuclear platinum(II) calix[4]-crown complex, [{Pt(*t*-Bu$_3$-tpy)}$_2$L](PF$_6$)$_2$ (**1**; *t*-Bu$_3$-tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine, L = 5,17-diethynyl-25,27-dimethoxycalix[4]crown-5). The molecular structure of **1** has been determined by X-ray crystallography, and its photophysical properties and chemosensing behavior have also been studied.

Complex **1** was synthesized by the reaction of [Pt(*t*-Bu$_3$-tpy)-Cl](OTf) and H$_2$L in dichloromethane in the presence of triethylamine and a catalytic amount of copper(I) iodide, followed by a metathesis reaction with NH$_4$PF$_6$ (Scheme 1). The structure of the complex cation of **1** in the solid state was depicted in Figure 1. The calixcrown ligand was found to adopt a cone conformation, with all the oxygen atoms on the calixarene unit pointing toward the same direction, namely toward the polyether crown moiety. The platinum(II) metal centers were arranged in an essentially square-planar geometry with some slight deviations in the bond angles from the idealized 90 and 180°, probably due to the coordination constraints imposed by the terpyridyl ligands (N(1)−Pt(1)−N(3), N(4)−Pt(2)−N(6), 160.7−161.4°, N(1)−Pt(1)−N(2), N(2)−Pt(1)−N(3), N(4)−Pt(2)−N(5) and N(5)−Pt(2)−N(6), 80.0−99.1°). The two platinum(II) terpyridyl moieties were connected to the alkynyl groups in a linear fashion with Pt−C≡C angles in the range of 175.4−178.3°. The Pt−C (1.98−2.02 Å) and C≡C (1.18−1.19 Å) bond lengths were comparable to those found in the related mononuclear platinum(II) alkynyl complexes.[7,9] The separation between the two platinum(II) metal centers was found to be 8.538 Å, indicating the absence of Pt−Pt or π−π interactions. It is likely that the presence of the polyether linkage at the lower rim of the calixarene, together with the presence of the sterically bulky *tert*-butyl groups on the terpyridyl ligands, would prevent the platinum metal centers from coming into close proximity.[7d,f]

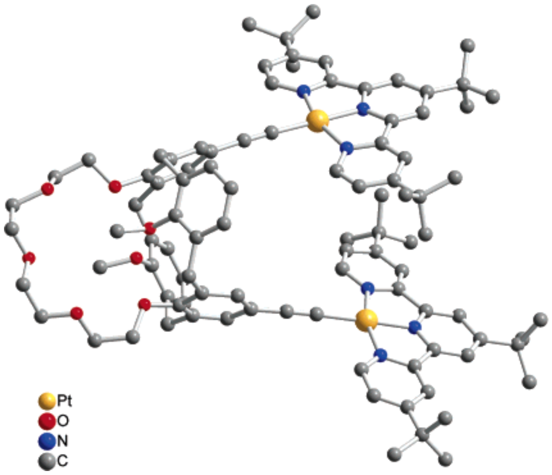


Figure 1. Perspective drawing of the complex cation of **1**. Hydrogen atoms and solvent molecules are omitted for clarity.

The electronic absorption spectrum of **1** in acetonitrile showed high-energy bands at about 264 nm, assigned as intraligand (IL) transitions of the calixcrown ligand. With reference to previous spectroscopic studies of the related platinum(II) alkynyl system,[7] the high-energy absorption bands at about 312−338 nm (with extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1}) were ascribed to intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the alkynyl and *tert*-butyl-terpyridyl moieties, mixed with some IL transitions of the calixcrown moieties, while the low-energy bands at 408−466 nm (with extinction coefficients in the order of 10^3 dm^3 mol^{-1} cm^{-1}) in the visible region were assigned to a [dπ(Pt) $\rightarrow$ π^*(*t*-Bu$_3$-tpy)] metal-to-ligand charge transfer (MLCT) transition, probably mixed with some [π(C≡CR) $\rightarrow$ π^*(*t*-Bu$_3$-tpy)] alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) character.

Upon excitation at $\lambda \geq 400$ nm, **1** displayed a weak emission band in acetonitrile solution at 738 nm. The long-lived emission with lifetimes in the microsecond range was suggestive of a triplet parentage. With reference to previous spectroscopic studies on other related terpyridyl platinum(II) alkynyl complexes,[7] the luminescence was assigned as derived from states of predominantly ^{3}MLCT [dπ(Pt) $\rightarrow$ π^*(*t*-Bu$_3$-tpy)] origin, probably mixed with some ligand-to-ligand charge transfer ^{3}LLCT [π(C≡C) $\rightarrow$ π^*(*t*-Bu$_3$-tpy)] character. This weakly emissive behavior can probably be attributed to the reductive quenching by photoinduced electron transfer (PET), in which the electron is transferred from the electron-rich alkoxy-substituted calixcrown moiety to the platinum terpyridyl unit that quenched the emissive ^{3}MLCT excited state, as well as energy transfer to the low-lying ^{3}LLCT state.[7a,c,d]

The complexation of complex **1** toward alkali-metal and alkaline-earth-metal ions was studied. The addition of Na$^+$ and Li$^+$ ions to a solution of **1** in acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$) resulted in an increase in the absorbance and a small blue shift in the absorption energy of the low-energy band. Well-defined

---

(9) (a) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261. (b) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Inorg. Chem.* **2001**, *40*, 3263. (c) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *Angew. Chem.* **2002**, *114*, 1951; *Angew. Chem., Int. Ed.* **2002**, *41*, 1871.

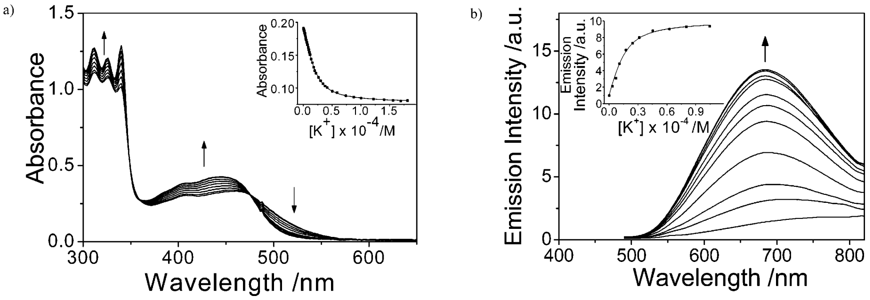


Figure 2. (a, left) UV/vis spectral changes of **1** upon addition of various concentrations of KPF_6 in CH_3CN (0.1 M $^{n}Bu_4NPF_6$). Inset: a plot of absorbance at 502 nm (■) as a function of the concentration of K^+ ions with theoretical fits. (b, right) Corrected emission spectral changes of **1** upon addition of KPF_6 in CH_3CN (0.1 M $^{n}Bu_4NPF_6$). Inset: a plot of emission intensity upon excitation at 475 nm (■) as a function of the concentration of K^+ with theoretical fits.

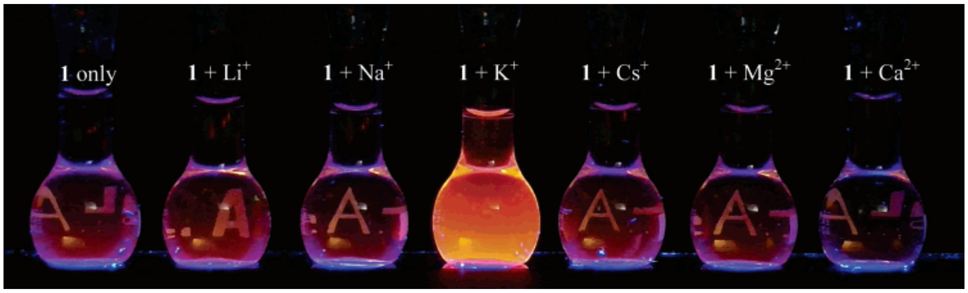


Figure 3. Photograph showing the effect of various metal ions (5.0×10^{-5} M) on the emission intensities of **1** (3.7×10^{-5} M) in CH_3CN (0.1 M $^{n}Bu_4NPF_6$).

isosbestic points were observed. Similar absorption changes were also observed upon addition of K^+ ions to **1**. Figure 2a shows the electronic absorption spectral traces of **1** in acetonitrile (0.1 M $^{n}Bu_4NPF_6$) upon addition of K^+ at 298 K. The inset shows the titration curve of **1** with K^+ ions together with the theoretical fits to the equation for the formation of a 1:1 adduct.[10] Stoichiometry studies indicated that **1** formed 1:1 complexes with the guest metal ions Li^+, Na^+, and K^+ under the conditions studied. This 1:1 complexation mode is further confirmed by the method of continuous variation,[11] as seen from the Job's plot, in which a break point at a mole fraction **1**/(**1** + K^+) of 0.5 was observed. The log *K* values for the binding of K^+, Na^+, and Li^+ ions to **1** were found to be 5.21, 2.73, and 1.11, respectively; the selectivity ratio of the complex for K^+ ion over Na^+ ion was about 3.01×10^2, and that for K^+ over Li^+ ion was 1.26×10^4. However, complex **1** showed no observable changes in the electronic absorption spectra upon addition of Mg^{2+} and Ca^{2+} ions, suggesting that the binding affinity of **1** toward Mg^{2+} and Ca^{2+} ions is very low or negligible.

The changes in the luminescence response of **1** toward Li^+, Na^+, and K^+ ions were also studied upon excitation at the isosbestic wavelengths of 460, 460, and 475 nm, respectively. In all cases, the emission spectra showed a blue shift in energy to ca. 635−685 nm upon inclusion of the respective Li^+, Na^+, and K^+ ions, with a concomitant substantial enhancement of the emission intensities, the effect of which is most prominent and sensitive in the case of K^+ ions. Figure 2b demonstrated the changes in emission intensity upon addition of K^+ ions. The inset in Figure 2b showed the emission titration curve of **1** with K^+ ions and the theoretical fits to the equation for the formation of a 1:1 adduct.[10] Similar to the cases for other alkynyl platinum(II) terpyridyl systems,[6,7] the emission origin was assigned to be derived from an excited state predominantly ^{3}MLCT in character with some mixing of a ^{3}LLCT state. The blue shift in emission energies upon cation inclusion could be rationalized by the lowering of the dπ(Pt) orbital energy as a result of the reduced electron-donating ability of the diethynylcalixcrown moiety upon inclusion of the guest metal ion, while the enhancement in the emission intensity was likely a consequence of the blocking of the intramolecular reductive electron transfer as well as energy transfer quenching pathways upon metal ion binding, since the unbound polyether linkage could be viewed as an alkoxy-substituted calixcrown moiety capable of acting as a good electron donor. Upon cation binding, its donor properties would be decreased and both the photoinduced electron transfer and energy transfer would no longer represent substantial quenching pathways. In addition, an increase in the rigidity of the calixcrown complex upon metal-ion binding would also result in the slowing down of nonradiative decay pathways, giving rise to an enhanced luminescence. The log *K* values of 1.04, 2.80, and 5.20 were obtained for the binding of Li^+, Na^+, and K^+ ions, respectively. The K^+/Na^+ and K^+/Li^+ selectivity ratios of 2.5×10^2 and 1.4×10^4, respectively, further suggest that **1** binds K^+ ions preferentially over Na^+ and Li^+ ions. These results are in good agreement with those obtained from UV/vis absorption binding studies and further support the 1:1 complexation mode. The improved selectivity in the present system compared to that in other related platinum(II) terpyridyl systems with crown ether pendants[6e,7a,b] is ascribed to the preorganized conformation of the calixcrown with high rigidity over the crown ether unit. A similar explanation was suggested by Cram and co-workers in the related organic counterparts.[3g−i]

An acetonitrile solution (0.1 M $^{n}Bu_4NPF_6$) of **1** (3.7×10^{-5} M) was weakly emissive in the absence of guest metal ions with a luminescence quantum yield of 1.1×10^{-4}. The emission intensity was only increased slightly ($\Phi_{\text{lum}} = 1.9 \times 10^{-4}$) in

---

(10) Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.

(11) (a) Jaffe, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; Wiley: New York, 1962. (b) Rohwer, H.; Collier, N.; Hoston, E. *Anal. Chim. Acta* **1995**, *314*, 219. (c) Peyman, A.; Uhlmann, E.; Wagner, K.; Augustin, S.; Weiser, C.; Will, D. W.; Breipohl, G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2809. (d) Reddy, A. C. P.; Sudharshan, E.; Rao, A. G. A.; Lokesh, B. R. *Lipids* **1999**, *34*, 1025.

the presence of a low concentration of Na^+ ion (5.0×10^{-5} M). However, in the presence of the same concentration of K^+ ion (5.0×10^{-5} M), the solution of **1** became strongly luminescent with a luminescence quantum yield of 1.3×10^{-3}. The much stronger enhancement of luminescence quantum yield upon coordination of K^+ ion (∼7-fold increase) in comparison to that of Na^+ ion (∼1.8-fold increase) further confirmed the higher selectivity of K^+ over Na^+ ion. At the same concentration of **1** (3.7×10^{-5} M) and in the presence of different metal cations, including Li^+, Na^+, K^+, Cs^+, Mg^{2+}, and Ca^{2+}, under identical conditions at a concentration of 5.0×10^{-5} M, only the reaction mixture with K^+ ions was strongly emissive (Figure 3). This visually distinguishable luminescent behavior for **1** in the presence of K^+ ions makes it a suitable candidate as a sensitive luminescence sensor for K^+ ions.

The present dinuclear platinum(II) calixcrown complex was shown to exhibit strong luminescence enhancement in the presence of K^+ ions, with selectivities 10^2-10^4-fold greater than those for Na^+, Li^+, and Cs^+ and alkaline-earth-metal ions such as Mg^{2+} and Ca^{2+}. The selective recognition of K^+ ions by the present system may find interesting applications in the design of luminescence chemosensors.

Acknowledgment. V.W.-W.Y. acknowledges support from the University Development Fund of The University of Hong Kong, The University of Hong Kong Foundation for Education Development and Research Limited, and the University Grants Committee Area of Excellence Scheme (Project No. AoE/P-10/01). The work described in this paper has been supported by a CERG grant from the Research Grants Council of the Hong Kong SAR, People's Republic of China (Project No. HKU 7120/02P). H.-S.L. acknowledges the receipt of a postgraduate studentship from The University of Hong Kong.

Supporting Information Available: Text detailing crystal data and refinement details for complex **1**, a figure giving a Job's plot experiment for the complexation ratio of complex **1** and K^+ ions, and a CIF file giving crystal data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060218F