Modular Cyclometalated Platinum(II) Complexes as Luminescent Molecular Sensors for pH and Hydrophobic Binding Regions

Kar-Ho Wong, Michael Chi-Wang Chan,* and Chi-Ming Che*[a]

Abstract: The photophysical properties of the ionisable cyclometalated platinum(II) complex [Pt(CNN)L]ClO_4, **1**-ClO_4 (HCNN = 6-phenyl-2,2′-bipyridine, L = Ph_2PCH_2NHPh) and its analogue [Pt(CNN)PPh_2CH_3]ClO_4, **2**-ClO_4 are investigated. The quantum yield of the ^{3}MLCT emission (MLCT = metal-to-ligand charge transfer) for **1** (λ_{max} 543 nm in acetonitrile at 298 K) is significantly lower than that for **2** due to photoinduced electron transfer (PET) quenching by the amine component. Complex **1** exhibits different emission intensities over a wide pH range in aqueous and micellar solutions based on the mechanism of PET suppression. The photoluminescence of **1** is employed to estimate the critical micelle concentration.

Keywords: electron transfer · luminescence · micelles · platinum · sensors

Introduction

Compared with luminescent octahedral d^6 metal species, coordinatively unsaturated luminophores such as square-planar d^8 platinum(II) derivatives can offer greater versatility in chemical sensing applications, because their geometry allow inner- and outer-sphere interactions with substrates. Hence, changes in photophysical behaviour have been observed in the presence of biomolecules,[1–5] gases and organic vapours.[6, 7] In this context, cyclometalated Pt^{II} complexes of 6-phenyl-2,2′-bipyridine and related ligands are important because they display emissive MLCT excited states in solution,[8-12] and these emissions are extremely environment-sensitive.[13] Meanwhile, the design of fluorescent chemosensors based on photoinduced electron transfer (PET) suppression is an area of continued interest in supramolecular chemistry.[14] While many organic examples of the versatile fluorophore-spacer-receptor system are known for the detection of protons, incorporation of an inorganic fluorophore component is rare.[15]

We now describe the use of the cyclometalated platinum(II) complex [Pt(CNN)L]ClO_4, **1**-ClO_4, as a sensitive luminescent pH probe. The aromatic amine moiety serves as a proton receptor, and is buffered from the phosphorus atom by a methylene spacer. The effects of protonation upon the excited-state properties of heterocycle-substituted platinum-1,2-enedithiolate complexes was recently described.[16]

Anionic microheterogeneous environments such as micelles can interact with a variety of ionic and hydrophobic substrates, and thus provide a surface/medium where precipitation and catalytic reactions can proceed.[17] The photochemistry of metal complexes in microheterogeneous surroundings has attracted considerable attention because of their diverse spectroscopic and redox properties.[18] Due to the hydrophobic nature of the CNN ‘head’ in the bifunctional complex **1**, a study of its photophysical responses in micellar solutions and at various pH is also presented.

Results and Discussion

Complex **1** and the analogue **2** without the amine module were prepared by treatment of Pt(CNN)Cl with the corresponding phosphane.[11] Complex **1** is sparingly soluble in aqueous media. The FAB mass spectra confirmed the presence of the molecular ion cluster, while ^{195}Pt satellites ($^1J_{Pt,P} \approx 3900$ Hz) were observed in the ^{31}P NMR spectra. The molecular structure of **1**-ClO_4 was determined by X-ray crystallography. The perspective view of **1** (Figure 1) illustrates the distorted square-planar geometry of the platinum centre, and the position of the amine moiety remote from the metal. The bond lengths and angles associated with the platinum atom are comparable to those found in [Pt(CNN)-PPh_3]ClO_4.[11a] The absence of close intermolecular Pt–Pt contacts between adjacent molecules (Pt–Pt > 4 Å) is attributed to the bulky nature of the ligand L which hinders the approach of d^8 metal ions.

---

[a] Prof. C. M. Che, Dr. M. C. W. Chan, K. H. Wong
Department of Chemistry, The University of Hong Kong
Pokfulam Road, Hong Kong
Fax: (+852) 2857-1586
E-mail: cmche@hkucc.hku.hk
mcwchan@hkusub.hku.hk

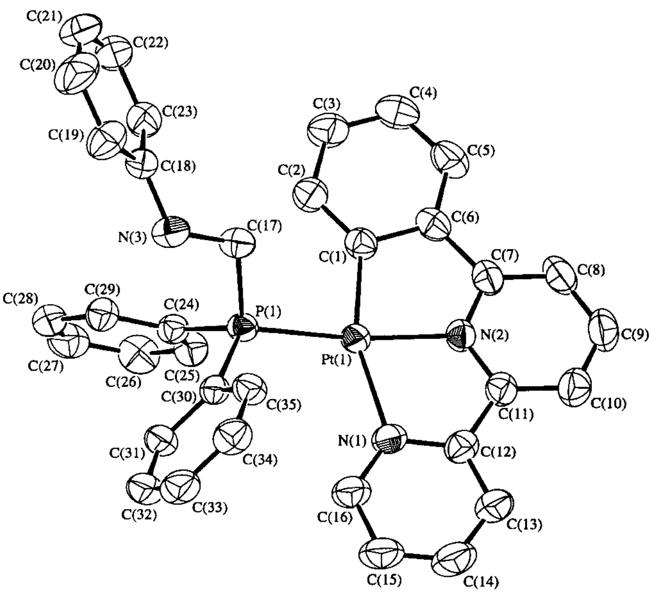


Figure 1. Perspective view of **1** (40% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Pt(1)–P(1) 2.247(1), Pt(1)–N(1) 2.149(4), Pt(1)–N(2) 2.013(4), Pt(1)–C(1) 2.024(5); N(1)-Pt(1)-C(1) 158.9(2), P(1)-Pt(1)-N(2) 169.8(1), C(17)-N(3)-C(18) 118.6(4).

Photophysical behaviour: The UV/Vis absorption spectra of **1** and **2** (Figure 2), like related cyclometalated platinum(II) species,[9–12] each contains several intense absorption bands at $\lambda < 350$ nm, arising from intraligand (IL) transitions of the CNN ligand, plus a broad and structureless absorption band in the visible region (400–500 nm, $\varepsilon = 1300\,\mathrm{dm^3 mol^{-1} cm^{-1}}$) which is ^{1}MLCT [(5d)Pt $\rightarrow \pi^*$(CNN)] in nature The absorption spectrum of **1** is pH independent, which is a requirement of luminescent PET proton sensors.

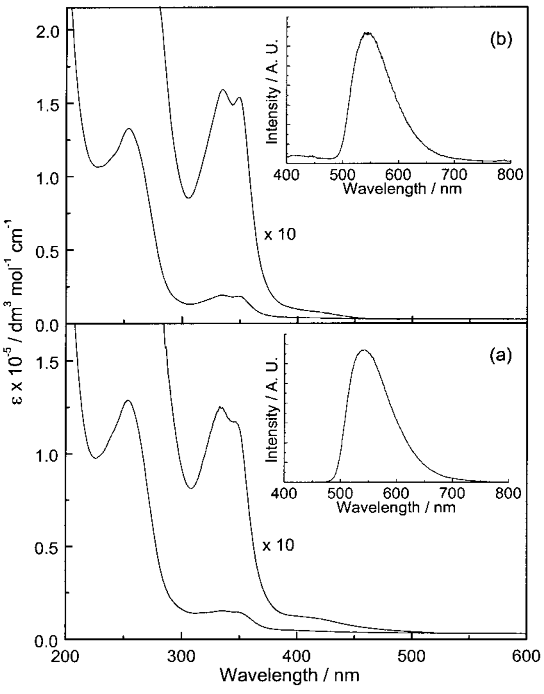
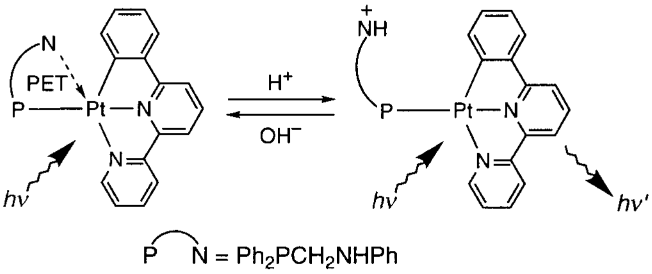


Figure 2. The absorption (inset: emission; $\lambda_{\mathrm{ex}} = 350$ nm) spectra of (a) **1** and (b) **2** in acetonitrile at 298 K.

Complex **1** is weakly emissive in polar solvents, and displays a weak emission band centred at 543 nm ($E_{\mathrm{ex}} = 350$ nm, $\tau = 88$ ns, $\Phi_{\mathrm{em}} = 0.001$) in acetonitrile at 298 K. This luminsescence is comparable to that observed for $[\mathrm{Pt(CNN)PPh_3}]^+$,[11a] and is assigned to a ^{3}MLCT excited state. Compound **2** has a significantly longer emission lifetime (0.26 μs) and a higher quantum yield (0.01). It is therefore apparent that a quenching process which provides an additional non-radiative decay pathway, namely PET, is occurring in **1**, with the aromatic amine group acting as an electron donor (Scheme 1). The emission of **1** and **2** in acetonitrile at 77 K are more intense, and display well-resolved vibronic structures with vibrational progressions of around 1200 cm^{-1}. Interestingly, the emission spectra of complex **2** are concentration-dependent in frozen acetonitrile. At low concentrations ($\approx 10^{-6}\,\mathrm{mol\,dm^{-3}}$), a high-energy vibronic emission at 527 nm is observed. Increasing the concentration of the complex results in a new red-shifted emission band centred at 635 nm. Indeed, at concentrations greater than $10^{-3}\,\mathrm{mol\,dm^{-3}}$, the emission at 527 nm is completely replaced the 635 nm band. Previous studies on $[\mathrm{Pt(tpy)Cl}]^+$ (tpy = 2,2′:6′,2″-terpyridine)[19] and related mono- and dinuclear Pt$^{\mathrm{II}}$ derivatives[11] indicate that the low energy emission band for **2** is ascribed to ligand–ligand (π–π) and/or metal–metal interactions.



Scheme 1. Proton-induced suppression of PET in complex **1**.

pH response: Due to efficient solvent-induced quenching, complex **1** shows much weaker emission ($\lambda_{\max} = 534$ nm) in water than in acetonitrile, with very low quantum yield ($\Phi_{\mathrm{em}} < 1 \times 10^{-4}$) and short emission lifetime ($\tau < 10$ ns). However, dramatic changes are seen in the emission spectra during pH titration. The emission intensity is noticeably enhanced in acidic media due to proton-induced suppression of PET, without variations in the energy or shape of the emission band (inset of Figure 3). Hence, as the amine receptor becomes protonated at low pH, quenching of the excited state is precluded (Scheme 1). Upon increasing the pH, quenching by PET is more prevalent and the minimum intensity is observed from pH 9. The quantum yield of complex **1** decreases from pH 1 to 9 with a proton-induced luminescence enhancement factor [LE factor = Φ(acid)/Φ(base)] of 130 (Figure 3). The pK_{a} value of 3.2 for **1**, estimated using by Equation 1,[14c] is comparable to those for related sensors bearing aromatic amine receptors.[15b, 20]

$$\log[(\Phi_{\max} - \Phi)/(\Phi - \Phi_{\min})] = \mathrm{pH} - \mathrm{p}K_{\mathrm{a}} \qquad (1)$$

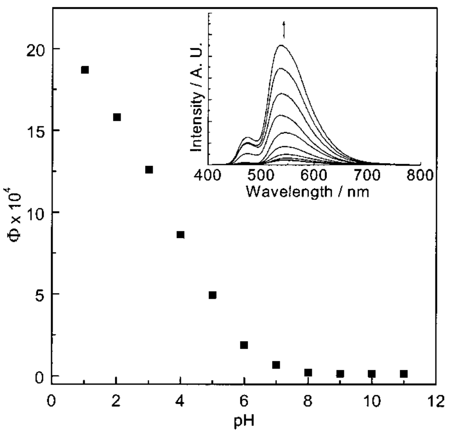


Figure 3. Variation of Φ versus pH for **1** (monitored at 534 nm, λ_{ex} = 350 nm, [**1**] = 1.3×10^{-5} mol dm^{-3}) in degassed H_2O at 298 K. Inset: Emission spectral traces for **1** at different pH in degassed H_2O (pH: 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1).

Responses in micellar solutions: Our studies in aqueous solutions reveal that the emissive properties of **1** are dependent on the concentration of sodium dodecyl sulfate (SDS). An emission at λ_{max} 581 nm is observed at low SDS concentrations below the critical micelle concentration (CMC),[21] where the solution becomes turbid with formation of a yellow precipitate. Low surfactant concentrations result in the SDS molecules acting as anions to precipitate complex **1**. When the CMC is reached, and at high SDS concentrations (> 10 mmol dm^{-3}), a clear solution develops and the original emission band at 534 nm is restored, but with considerable enhancement. Under these conditions, micellar assemblies are formed with the hydrophobic CNN head of the complex embedded inside or at the surface of the aggregates. Hence the ability of molecule **1** to sense hydrophobic binding regions, where solvent-induced quenching is suppressed, is demonstrated by the observed luminescence enhancement. Furthermore, complex **1** can be utilised to estimate the CMC. Figure 4 shows a plot of the emission intensity of the MLCT band at 534 nm against SDS concentration. The emission intensity increases sharply between 7 and 9 mmol dm^{-3}, and reaches saturation at 12 mmol dm^{-3}.[22] The photoluminescence of **1** therefore offers a convenient optical method to assess the CMC[23] and probe conformational changes of aqueous micelles in different environments.

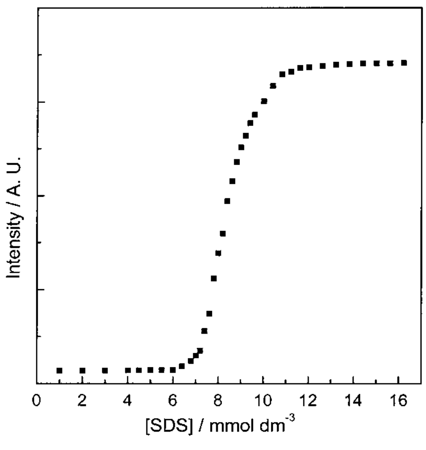


Figure 4. Variation of luminescence intensity versus [SDS] for **1** (monitored at 534 nm, λ_{ex} = 350 nm, 298 K, [**1**] = 1.3×10^{-5} mol dm^{-3}).

The emission intensity of complex **1** is also pH-dependent in micellar solutions above CMC (Figure 5). In basic solutions, minor changes are observed; the luminescence is quenched because the unprotonated amine moiety can engage in PET to the Pt^{II} centre. As the pH decreases, the emission at 534 nm becomes significantly enhanced and the strongest emission is detected in highly acidic medium (pH 1). A proton-induced LE factor of 7 is obtained, which is smaller than that in the absence of micellar aggregates (130).

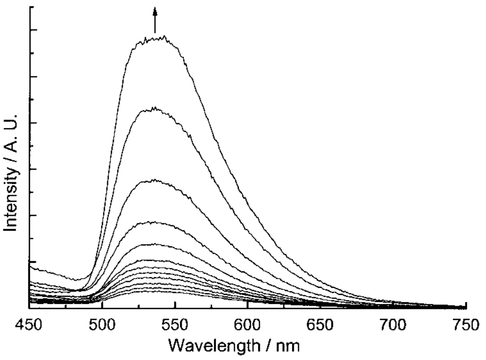


Figure 5. Emission spectral traces of **1** at different pH in 0.01 mol dm^{-3} SDS solution at 298 K (pH: 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1; λ_{ex} = 350 nm).

Conclusion

The present work highlights a bifunctional platinum(II) spectroscopic probe for pH and hydrophobic binding regions, based upon the luminescence enhancement of complex **1** at low pH and in the presence of SDS micelles. The flexibility of these fluorophore-spacer-receptor systems and the versatility of the synthetic routes to functionalised cyclometalated platinum(II) derivatives will enable one to pursue new optical sensors with applications for studying the dynamics of macromolecules and biological substrates.

Experimental Section

General procedures: The solvents were purified according to standard methods.[24] K_2PtCl_4, diphenylphosphane, methyldiphenylphosphane and SDS were obtained from commercial sources and used as received. Pt(CNN)Cl[11] was prepared by literature methods. ^{1}H, and ^{31}P NMR spectra were recorded on a DPX-300 Bruker FT-NMR spectrometer with chemical shift (in ppm) relative to tetramethylsilane (^{1}H) and external H_3PO_4 (^{31}P). Elemental analyses were performed by Butterworth Laboratories Ltd, UK. UV/Vis spectra were recorded on a Perkin Elmer Lambda 19 UV/Vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-2 Model F11 fluorescence spectrophotometer. Absolute emission quantum yields were measured by the optical dilute method developed by Demas and Crosby,[25] and an aqueous solution of [Ru(bpy)$_3$]Cl$_2$ (Φ = 0.042) was used as standard.

Synthesis: Ph_2PCH_2NHPh, L: A report by Balch et al was modified.[26] Diphenylphosphane (1.1 g, 5.92 mmol) was added to a mixture of aniline (0.55 g, 5.92 mmol) and paraformaldehyde (0.5 g) in toluene (30 mL) at 65 °C under nitrogen, and stirred for 4 h until all solids were dissolved. This solution was allowed to cool, then filtered and concentrated to yield a colourless oily solid. This was dissolved in dichloromethane (10 mL) and ethanol (30 mL), then cooled to $-20\,^{\circ}C$ for 12 h. The resultant white crystalline solid was washed with ethanol and air-dried. Yield: 1.12 g, 65%. Elemental analysis (%) calcd for $C_{19}H_{18}NP$ (291.33): C 78.33, H 6.23, N 4.81; found C 78.14, H 6.45, N 4.93; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.51-6.65$ (m, 15H, aryl H), 3.82 (d, 2H, $^2J_{P,H} = 3.7$ Hz, CH_2); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): $\delta = -18.16$; MS-EI: m/z (%): 291 (100) [M^+].

[Pt(CNN)L]ClO$_4$ [1-ClO$_4$]: Ligand L (0.06 g, 0.22 mmol) was added to a suspension of Pt(CNN)Cl (0.10 g, 0.22 mmol) in acetonitrile (20 mL) and the mixture was stirred for 2 h to give a clear yellow solution. Excess $LiClO_4$ was added to yield a yellow precipitate, which was collected and washed with diethyl ether. Recrystallisation by vapour diffusion of diethyl ether into an acetonitrile solution afforded yellow crystals. Yield 0.13 g, 70%. Elemental analysis (%) calcd for $C_{35}H_{29}N_3O_4ClPtP$ (817.15): C 51.45, H 3.58, N 5.14; found C 51.40, H 3.62, N 5.20; ^1H NMR (300 MHz, CD_3CN): $\delta = 8.88-6.69$ (m, 26H, aryl H), 4.76 (d with ^{195}Pt satellites, 2H, $^2J_{P,H} = 3.3$ Hz, $^3J_{Pt,H} = 28.5$ Hz, CH_2); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): $\delta = 15.06$ ($^1J_{Pt,P} = 3937$ Hz); MS-FAB: m/z (%): 717 (100) [M^+]; UV/Vis (CH_3CN): λ_{max} (ε) = 254 (130 000), 335 (12 000), 400–500 (1300).

[Pt(CNN)(PPh$_2$CH$_3$)]ClO$_4$ [2-ClO$_4$]: The same procedure for **1**-ClO$_4$ was used except L was replaced by methyldiphenylphosphane. Yield 0.14 g, 85%. Elemental analysis (%) calcd for $C_{29}H_{24}N_2O_4ClPtP$ (726.04): C 47.98, H 3.33, N 3.86; found: C 48.05, H 3.40, N 3.94; ^1H NMR (300 MHz, CD_3CN): $\delta = 8.17-6.81$ (m, 21H, aryl H), 2.52 (d with ^{195}Pt satellites, 3H, $^2J_{P,H} = 10.0$ Hz, $^3J_{Pt,H} = 43.6$ Hz, CH_3); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): $\delta = 7.33$ ($^1J_{Pt,P} = 3906$ Hz); MS-FAB: m/z (%): 626 (100) [M^+]; UV/Vis (CH_3CN): λ_{max} (ε) = 254 (130000), 335 (15000), 400–450 (1100).

X-ray crystallographic data for 1-ClO$_4$: $\{[C_{35}H_{29}N_3PPt]^+ClO_4^-\}$; formula weight = 817.15, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.034(3)$, $b = 16.529(8)$, $c = 9.576(3)$ Å, $\alpha = 99.33(1)$, $\beta = 114.98(2)$, $\gamma = 86.72(4)^{\circ}$, $V = 1562(5)$ Å^3, $Z = 2$, $\rho_{cacld} = 1.737$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 46.55$ cm^{-1}, $F(000) = 804$, $2\theta_{max} = 50^{o}$, $T = 301$ K. A yellow crystal of dimensions $0.15 \times 0.08 \times 0.25$ mm was used for data collection on a Rigaku AFC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) using $\omega-2\theta$ scans. Intensity data (three standard reflections measured after every 300 reflections showed decay of 1.19%) were corrected for decay and for Lorentz and polarisation effects, and absorption corrections (transmission min 0.532; max 1.000) were made. A total of 5582 reflections were measured, of which 5508 were unique ($R_{int} = 0.027$). The structures were solved by Patterson methods, expanded by Fourier methods (PATTY[27]) and refined by full-matrix least-squares using the software package TeXsan[28] on a Silicon Graphics Indy computer. One formula unit constitutes a crystallographic asymmetric unit. The perchlorate anion was disordered and the O atoms placed in eight positions with occupation numbers O(1) 1.0; O(2) and O(2′) 0.7 and 0.3; O(3) and O(3′) 0.55 and 0.45; O(4), O(4′) and O(4″) 0.45, 0.25 and 0.3, respectively. All 41 non-hydrogen atoms were refined anisotropically and the disordered O atoms were refined isotropically. The positional parameters of H(1) located in the difference Fourier maps were refined and 28H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 405 variable parameters by least-squares refinement on F with $w = 4\ F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.014\,F_o^2)^2]$ for 4680 reflections with $I > 3\sigma(I)$ was reached at $R = 0.028$ and $wR = 0.030$ with a goodness-of-fit of 1.60. $(\Delta/\sigma)_{max} = 0.03$ for atoms of the complex cation. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.71 and 0.87 e Å^{-3}, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-102481. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful for support from The University of Hong Kong and the Research Grants Council of the Hong Kong Speical Administrative Region, China [HKU 7298/99P]. Dr. K. K. Cheung is acknowledged for the X-ray structural determination.

[1] a) S. J. Lippard, *Acc. Chem. Res.* **1978**, *11*, 211–217; b) J. K. Barton, S. J. Lippard, *Biochemistry* **1979**, *18*, 2661–2668; c) M. Howe-Grant, S. J. Lippard, *Biochemistry* **1979**, *18*, 5762–5769; d) J. C. Dewan, S. J. Lippard, W. R. Bauer, *J. Am. Chem. Soc.* **1980**, *102*, 858–860.

[2] W. D. McFadyen, L. P. G. Wakelin, I. A. G. Roos, B. L. Hillcoat, *Biochem. J.* **1987**, *242*, 177–183.

[3] H. Q. Liu, S. M. Peng, C. M. Che, *J. Chem. Soc., Chem. Commun.* **1995**, 509–510.

[4] a) G. Arena, L. Monsú Scolaro, R. F. Pasternack, R. Romeo, *Inorg. Chem.* **1995**, 34, 2994–3002; b) L. Monsú Scolaro, A. Romeo, A. Terracina, *Chem. Commun.* **1997**, 1451–1452.

[5] C. S. Peyratout, T. K. Aldridge, D. K. Crites, D. R. McMillin, *Inorg. Chem.* **1995**, *34*, 4484–4489.

[6] Y. Kunugi, K. R. Mann, L. L. Miller, C. L. Exstrom, *J. Am. Chem. Soc.***1998**, *120*, 589–590.

[7] W. W. S. Lee, K. Y. Wong, X. M. Li, *Anal. Chem.* **1993**, *65*, 255–258.

[8] a) L. Chassot, E. Müller, A. von Zelewsky, *Inorg. Chem.* **1984**, *23*, 4249–4253; b) M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet, A. von Zelewsky, *Chem. Phys. Lett.* **1985**, *122*, 375–379; c) D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. von Zelewsky, *J. Am. Chem. Soc.* **1987**, *109*, 7720–7724.

[9] C. W. Chan, T. F. Lai, C. M. Che, S. M. Peng, *J. Am. Chem. Soc.* **1993**, *115*, 11245–11253.

[10] C. W. Chan, L. K. Cheng, C. M. Che, *Coord. Chem. Rev.* **1994**, *132*, 87–97.

[11] a) T. C. Cheung, K. K. Cheung, S. M. Peng, C. M. Che, *J. Chem. Soc. Dalton Trans.* **1996**, 1645–1651; b) S. W. Lai, M. C.-W. Chan, T. C. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* in press..

[12] a) M. C. Tse, K. K. Cheung, M. C. W. Chan, C. M. Che, *Chem. Commun.* **1998**, 2295–2296; b) S. W. Lai, M. C. W. Chan, S. M. Peng, C. M. Che, *Angew. Chem.* **1999**, *111*, 708–710; *Angew. Chem. Int. Ed.* **1999**, *38*, 669–671; c) S. W. Lai, M. C. W. Chan, K. K. Cheung, C. M. Che, *Organometallics*, in press.

[13] a) L. Z. Wu, T. C. Cheung, C. M. Che, K. K. Cheung, M. H. W. Lam, *Chem. Commun.* **1998**, 1127–1128; b) H. Q. Liu, T. C. Cheung, C. M. Che, *Chem. Commun.* **1996**, 1039–1040.

[14] a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; b) *Fluorescent Chemosensors for Ion and Molecule Recognition* (Ed. A. W. Czarnik), American Chemical Society, Washington DC, **1993**; c) R. A. Bissell, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, K. R. A. S. Sandanayake, *Chem. Soc. Rev.* **1992**, *21*, 187–195.

[15] Based on $[Ru(bpy)_3]^{2+}$: a) R. Grigg, J. M. Holmes, S. K. Jones, W. D. J. A. Norbert, *J. Chem. Soc. Chem. Commun.* **1994**, 185–187; b) R. Grigg, W. D. J. A. Norbert, *J. Chem. Soc. Chem. Commun.* **1992**, 1300–1302. Lanthanide derivatives: c) A. P. de Silva, H. Q. N. Gunaratne, T. E. Rice, *Angew. Chem.* **1996**, *108*, 2253–2255; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2116–2118; d) T. Gunnlaugsson, D. Parker, *Chem. Commun.* **1998**, 511–512.

[16] a) S. P. Kaiwar, A. Vodacek, N. V. Slough, R. S. Pilato, *J. Am. Chem. Soc.* **1997**, *119*, 3311–3316; b) S. P. Kaiwar, A. Vodacek, N. V. Slough, R. S. Pilato, *J. Am. Chem. Soc.* **1997**, *119*, 9211–9214.

[17] J. H. Fendler, *Chem. Rev.* **1987**, *87*, 877–899.

[18] a) K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, New York, **1987**; b) H. H. Thorp, C. V. Kumar, N. J. Turro, H. B. Gray, *J. Am. Chem. Soc.* **1989**, *111*, 4364–4368; c) M. H. Gehlen, F. C. De Schryver, *Chem. Rev.* **1993**, *93*, 199–221; d) C. Turro, S. Niu, S. H. Bossmann, D. A. Tomalia, N. J. Turro, *J. Phys. Chem.* **1995**, *99*, 5512–5517; e) M. R. Arkin, E. D. A. Stemp, C. Turro, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.* **1996**, *118*, 2267–2274.

[19] J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4591–4599.

[20] A. P. de Silva, R. A. D. D. Rupasinghe, *J. Chem. Soc. Chem. Commun.* **1985**, 1669–1670.

[21] J. H. Fendler, E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, **1975**. For SDS at 25 °C, CMC = 8.1 mM, $A = 62$.

[22] The pH variation during this experiment was ±0.1 which did not affect the emission intensity.

0947-6539/99/0510-2848 $ 17.50+.50/0

[23] For an earlier example, see: J.-C. Chambron, J.-P. Sauvage, *Chem. Phys. Lett*. **1991**, *182*, 603 – 607.

[24] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, **1980**.

[25] J. N. Demas, G. A. Crosby, *J. Phys. Chem*. **1971**, *75*, 346.

[26] A. L. Balch, M. M. Olmstead, S. P. Rowley, *Inorg. Chim. Acta* **1990**, *168*, 255 – 264.

[27] PATTY: P. R. Beurskens, G. Admiraal, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla (**1992**). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

[28] TeXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, (**1985** & **1992**).

Received: February 18, 1999 [F 1622]