

Figure 1. Observed Ru K edge EXAFS spectra, extracted oscillations, and associated Fourier transforms of (a) Ru/ γ -Al₂O₃ reduced at 723 K in H₂, (b) after admission of 200 Torr CO, and (c) Ru powder. All the spectra were obtained at room temperature.

solution in a flow of nitrogen at room temperature onto γ -Al₂O₃, which had been pretreated by heating at 773 K in air for 10 h and under vacuum for 2 h. Then the solvent was removed in a flow of nitrogen at 323 K. The catalyst thus obtained was pressed into a self-supporting disk and was placed in an in situ EXAFS cell with Be windows and a heater. The decomposition of Ru₃(CO)₁₂ supported on γ -Al₂O₃ was carried out under vacuum at 723 K for 2 h. Then the catalyst was reduced with hydrogen at 723 K for 2 h, followed by evacuation at the same temperature for 1 h. The sample was kept in the vacuum tight cell in order to minimize the possible effect of water.⁶ The dispersion of the catalyst was estimated to be 0.8 from the hydrogen chemisorption. The EXAFS measurements were performed by a double crystal X-ray spectrometer equipped with Ge(444) and LiF(220) bent crystals, which will be reported elsewhere.⁷

Figure 1a shows the Ru K EXAFS spectrum, extracted oscillation, and the associated k^3 -weighted Fourier transform of the reduced 2 wt % Ru/ γ -Al₂O₃ catalyst. For comparison, those of Ru powder as a reference are shown in Figure 1c. The long EXAFS oscillation of the catalyst is characteristic of heavy elements and clearly shows that the neighbor atoms around Ru are also Ru, but its amplitude and consequently the peak intensity in the associated Fourier transform are much weaker than those of bulk Ru, indicating that Ru clusters are highly dispersed. A shoulder of the main peak in the Fourier transform may come from the oxygen atoms of the support. From the least-squares curve fitting⁸ by the use of the theoretical scattering amplitude and phase factor by Teo and Lee,⁹ the Ru-Ru interatomic distance in the cluster is determined to be 2.55 Å, which is shorter than the bulk value by as much as 0.13 Å, and the coordination number is about 4, which is significantly smaller than the bulk value of 12. Smaller coordination numbers^{8,10} and shorter interatomic

distances^{11,12} have often been observed in very small metal clusters. Reduction in the coordination number is due to the surface effect and can be employed to estimate cluster sizes.⁹ If three-dimensional hcp structure of the bulk metal is assumed, a cluster consisting of about 7 atoms has coordination number close to 4.

The adsorption of CO on the catalyst thoroughly changes the local structure around Ru atoms as evidenced in the EXAFS spectrum shown in Figure 1b. Compared with spectrum a, the oscillation decreases very rapidly with increasing k values, which means that now the neighboring atoms around Ru are not heavy elements but light ones. The associated Fourier transform shows two peaks which should be assigned to Ru-C and Ru-O of the adsorbed CO molecule. Due to the uncertainty of the electron mean free path in this system the coordination number of CO could not be determined, while the CO/Ru ratio of 1.2 was obtained from the chemisorption study. The spectrum does not change by vacuum pumping at room temperature, but the same spectrum as in Figure 1a is reproduced after heating the sample to 573 K while evacuating. The spectrum change between spectrum a and spectrum b is completely reversible by repeated adsorption/desorption cycles.

The following conclusions can be drawn from the present study. First, ultradispersed Ru clusters are formed on alumina support from Ru₃(CO)₁₂. Second, Ru-Ru bonds in the very tiny Ru clusters are disrupted by CO adsorption, leading to the formation of a new species like Ru(CO)_n. Third, the tiny Ru clusters are recovered by CO desorption.

These findings are closely related to those reported on Rh, and they suggest that the disruption of metal-metal bonds in tiny clusters upon adsorption of CO is a ubiquitous phenomenon. Since it is unlikely that decomposition takes place in large metal particles or single crystal, this might supply a clue to the understanding of dependences of selectivity and activity on particle size in catalytic reactions.⁵

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Chelation-Enhanced Fluorescence in 9,10-Bis(TMEDA)anthracene

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Received February 8, 1988

We wish to report that the fluorescence emission intensity of a structurally simple anthracene derivative, 9,10-bis(TMEDA)-anthracene² (**1**), increases over 1000-fold in the presence of zinc chloride. The mechanism by which this *chelation-enhanced fluorescence* (CHEF) occurs indicates that fluorescence detection of metal ions is possible by using structurally simple conjugates between fluorescent molecules and nitrogenous ligands.

In 1986, we reported the synthesis and characterization of anthracene **1** and its binuclear zinc chloride complex (**2**).³ During the course of our work, we observed that acetonitrile solutions of compound **1** did not exhibit the high fluorescence characteristic of, for example, 9,10-dimethylantracene; however, acetonitrile solutions of compound **2** were strongly fluorescent (blue) when irradiated with a long-wavelength UV light source. A survey of

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(1) Recipient of an Ohio State University graduate fellowship.

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Table I. Relative Fluorescence Emission Intensities of Compounds **1**, **2**, and 9,10-Dimethylanthracene (DMA) under Various Conditions

compd ^a	solvent	added [TMEDA] (M × 10 ⁴)	added [ZnCl ₂] (M × 10 ⁴)	rel inten at 427 nm ^b
1	1	CH ₃ CN		1.6 ^c
2	2	CH ₃ CN		527
3	2	CH ₃ CN	20	0.4
4	DMA	CH ₃ CN		960
5	DMA	CH ₃ CN	2	960
6	DMA	CH ₃ CN	20	905
7	DMA	CH ₃ CN	200	70
8	DMA	CH ₃ CN	2000	22
9	DMA	CH ₃ CN	4000	12
10	1	H ₂ O, pH 11.7		2.5 ^d
11	1	H ₂ O, pH 10.0		2.4 ^d
12	1	H ₂ O, pH 8.0		3.0 ^d
13	1	H ₂ O, pH 6.5		4.5 ^d
14	1	H ₂ O, pH 4.0		114 ^d
15	1	H ₂ O, pH 1.6		895 ^d
16	1	CH ₃ CN	0.5	19
17	1	CH ₃ CN	1.0	82
18	1	CH ₃ CN	1.5	179
19	1	CH ₃ CN	2.0	339
20	1	CH ₃ CN	2.5	444

^aThe concentration of all anthracenes was 1×10^{-4} M. ^bAll intensities are estimated to be $\pm 10\%$. The excitation wavelength was 335 nm in CH₃CN, 345 nm in aqueous solutions. ^cThis value represents an upper limit for the relative fluorescence intensity of compound **1**; in fact, the shape of the emission spectrum of our sample of **1** is quite different than that of either **2** or DMA. The observed fluorescence may, to an undetermined extent, be due to a trace fluorescent impurity. ^dA 340 nm long pass filter was used when acquiring the fluorescence data of the aqueous solutions; thus, intensity values are not comparable with those of acetonitrile solutions. Values obtained in aqueous solution are internally comparable.

the literature reveals that the use of fluorescence to analyze for the presence of metal ions is a well-precedented technique.^{4,5} Furthermore, work over the past 11 years by the laboratories of Sousa⁶ and others⁷ have shown that the known ion complexing properties of crown and azacrown ethers may be used to design chelating fluorophores whose emission spectra change upon the addition of metal ions. Most recently, Masilamani, Lucas, and Morgan have found that the fluorescence of 4-methylcoumaro-[2.2.2]- and [2.1.1]cryptands is enhanced on complexation with potassium and lithium ion, respectively.⁸ While the application of chelation-enhanced fluorescence holds great promise as an analytical tool, emission intensity enhancements reported to date have not been extremely large, ranging to a 47-fold increase in the best case. Because we have observed such an atypically large enhancement using anthracene **1** (greater than 1000-fold), our results suggest both that structurally simple conjugates between ligands and fluorophores can afford a CHEF and that the sensitivity of CHEF methods may potentially be much greater than previously considered.

The chelation of zinc chloride to bis(TMEDA)anthracene (**1**) dramatically enhances the observed fluorescence, as can be seen

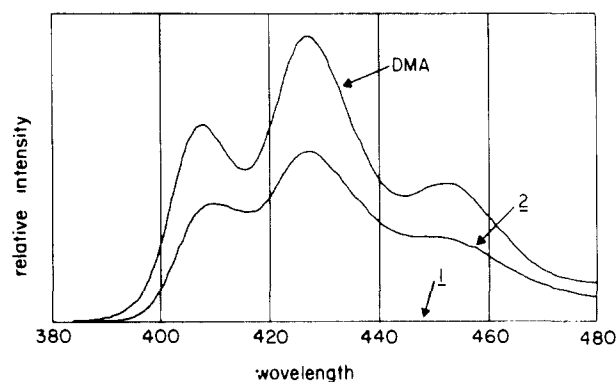
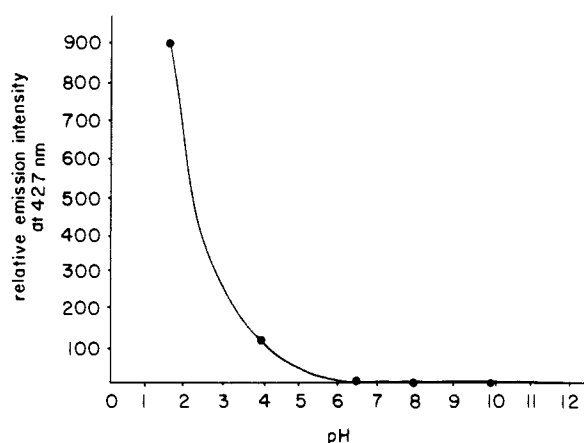
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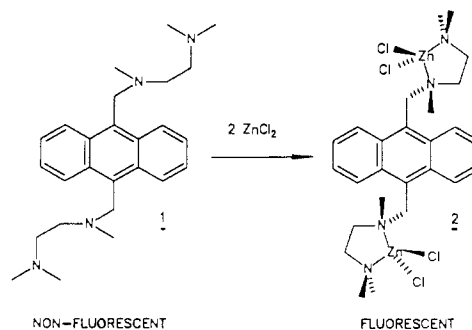
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**Figure 1.** Fluorescence emission spectra of compounds **1**, **2**, and 9,10-dimethylanthracene (DMA) in acetonitrile (all 10^{-4} M solutions).**Figure 2.** Fluorescence emission intensity of 10^{-4} M compound **1** in water as a function of pH.

by comparing entries 1–3 of Table I. Entry 1 provides an upper limit for the fluorescence of compound **1**; in fact, some or all of this fluorescence may be due to a trace impurity present in compound **1**. Instead, we use as our references the relative intensities of crystallized compound **2** (entry 2) and the same sample to which 20 equiv of TMEDA have been added (entry 3). When this large excess of competing ligand is present, the emission intensity drops by a factor of over 1000. While both the intensity and shape of compound **2**'s emission spectrum closely match that of 9,10-dimethylanthracene (Figure 1), some of compound **2** is likely dissociated even in the absence of added TMEDA; the intrinsic fluorescence intensity is consequently even higher than that indicated by entry 2.



What can account for this very large change in the fluorescence emission intensity? We believe we are simply observing fluorescence quenching via exciplex formation, made very efficient in compound **1** by the high effective concentration of the intramolecular amine groups. Fluorescence quenching by inter- and intramolecular amines is, of course, a well-known phenomenon,⁹

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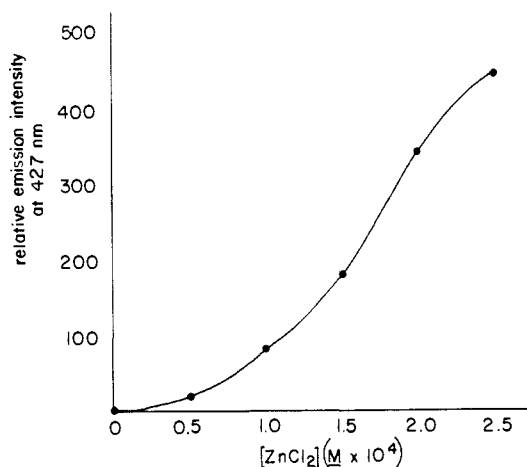


Figure 3. Fluorescence emission intensity of 10^{-4} M compound **1** in acetonitrile as a function of added ZnCl_2 .

and as seen in entries 4–9 the fluorescence of 9,10-dimethylanthracene is quenched by addition of TMEDA. At $[\text{DMA}] = 0.1$ mM, 4000 equiv of added TMEDA result in quenching by a factor of 80; the intramolecular quenching at the same concentration of compound **1** with no added TMEDA is roughly 30-times more efficient¹⁰ than even this.

Consequently, we explain the observed CHEF in 9,10-bis(TMEDA)anthracene by noting that, when chelated to a metal ion, the amine lone pairs become involved in bonding and are unable to donate an electron to the excited state of the anthracene. This explanation, which has been suggested previously,^{7d,e} is corroborated by the pH profile shown in entries 10–15 of Table I (shown graphically in Figure 2) obtained in aqueous solution. At pH 11.7, the amine groups are almost completely unprotonated and the fluorescence of compound **1** is very low; at pH 1.6, most of the amines are protonated, and the fluorescence increases by a factor of over 300. Entries 16–20 indicate that in acetonitrile, the fluorescence increase may be titrated by addition of metal ion (Figure 3).¹¹ Solubility limits prevent us from further raising the metal ion concentration and therefore determining an asymptotic “intrinsic fluorescence” for complex **2**, which is partially dissociated even in acetonitrile saturated with ZnCl_2 (entry 20). The same titration done in aqueous solution fails; it is not surprising that the complexation of zinc ion with **1** in water is not complete at equimolar concentrations. Cryptands leading to polydentate chelation will provide much larger association constants.

These results predict that nitrogen-containing ligands with known specificities for metal ions may be utilized as fluorescent probes via a simple, flexible connection to a fluorescent compound such as anthracene. Complexation need not change the conformation of the fluorophore, as required by an “inhibition of vibrational decay” mechanism, but it must tie up amine lone pairs. Indeed, it may be possible to tie up amine lone pairs in other interesting ways, such as ion-pairing or strong hydrogen bonding; each interaction suggests potential analytical applications. Furthermore, the great distance through which electron transfer may occur suggests that amine and fluorophore groups need not be proximal to one another. We believe this approach to the design of fluorescent analytical probes has considerable potential and

(10) Comparing the relative intensity of 9,10-bis(TMEDA)anthracene (entry 3) with that of 9,10-dimethylanthracene plus 4000 equiv of TMEDA (entry 9).

(11) The emission intensity of **1** plus 2 equiv of ZnCl_2 is less than that of preformed **2**. We attribute this primarily to the fact that ZnCl_2 is hygroscopic; hydration will increase its apparent molecular weight and thereby decrease the actual concentration of added zinc. Binuclear complex **2** has been shown to be anhydrous by microanalysis (cf. ref 3); this is expected inasmuch as TMEDA complexation is known to provide a source of anhydrous zinc chloride (Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* 1977, 679). While the CHEF of a different complex is reported to be diminished by the addition of water to the acetonitrile solution (cf. ref 7f), we observe a small (15%) increase upon addition of 1×10^{-2} M water to the solution described in entry 2, Table I.

are continuing our work on this topic.

Acknowledgment. We gratefully acknowledge support for this work from the National Science Foundation and from The Ohio State University in the form of a graduate fellowship to one of us (M.E.H.). Shared resources, including the use of a fluorimeter, were made available by Prof. M. Platz of this department. FT NMR spectra were obtained with equipment funded in part by NIH Grant No. 1 S10 RR01458-01A1. We are particularly appreciative for the highly constructive suggestions of several reviewers.

Electrocyclic Reactions of 13-*cis*-Retinal Schiff Bases

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Received March 17, 1988

Bacteriorhodopsin, the protein that functions as a photochemical proton pump coupled to ATP synthesis in the purple membrane of *Halobacterium halobium*, consists of retinal bound to a lysine residue via a Schiff base linkage.¹ Protonation–deprotonation of the retinal Schiff base nitrogen and *cis*–*trans* isomerization of its Δ^{13} double bond are considered to be intimately involved in the proton pump photocycle.² As a spectroscopic model for bacteriorhodopsin, Schiff base derivatives of *all-trans*-retinal (**1a**) and 13-*cis*-retinal (**2a**) have been studied extensively, especially in terms of their electronic and vibrational absorption characteristics.³ Synthetic investigations in this laboratory have allowed access to a variety of side chain analogues^{4a-c} of retinal, and we have accordingly initiated a systematic investigation of the chemical and spectroscopic properties of the corresponding Schiff bases, in both their protonated and deprotonated forms. It is the purpose of this communication to report the extraordinarily facile six-electron electrocyclicization⁵ of Schiff bases of 13-*cis*-retinal

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