Intermolecular Excimer Formation in Dinuclear Metal Complexes

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In this paper the intramolecular/intermolecular excimer formations of $[Fe_2(bpmp)(1\text{-}pyace)_2](BF_4)_2$, $[ZnFe(bpmp)(1\text{-}pyace)_2](ClO_4)_2$ and $[Zn_2(bpmp)(1\text{-}pyace)_2]ClO_4$ which contain 1-pyreneacetic acid as a chromophore are reported. The fluorescent properties of the ZnZn complex offer the intramolecular dimers of the two chromophores in addition to intermolecular dimers due to the intermolecular stacking. The ZnFe and FeFe complexes are under the strong influence of quenching and show weak intramolecular/intermolecular excimer formation in the concentration more than 10^{-4} M. The emission intensities and intensity ratios (I_E/I_M) of the fluorescence are dependent on the metal ions.

The quenching of singlet and triplet excited states of aromatic hydrocarbons in coordination complexes is the subject of intense investigations.[1-5] Photoinduced electron transfer and electron energy transfer are thought as the main deactivation pathways responsible for efficient fluorescence or phosphorescence inhibitions. It is important to make clear the pathways to study fluorescence chemistry of transition-metal complexes containing chromophore, because transition-metal complexes and these supramolecular systems have found applications of interest in the area of metal ion sensing,[6] photocatalysis[7] and etc. This paper was carried out to make sure a role of transition metal ions in fluorescence chemistry. The complexes shown in chart 1 were prepared according to the method described elsewhere,[8] where Hbpmp is 2,6-bis[bis-(2-pyridylmethyl)-aminomethyl]-4-methylphenol and 1-pyac is 1-pyreneacetic acid (**1**). Analytically pure samples were obtained. The FAB-Mass spectrum of $[Fe_2(bpmp)(1\text{-}pyace)_2](BF_4)_2$ **FeFe(1)** shows peaks at m/z=1246.7 calculated for$[Fe_2(bpmp)(1\text{-}pyace)_2]BF_4^+$, m/z=1159.6 calculated for$[Fe_2(bpmp)(1\text{-}pyace)_2]^+$ and m/z=579.8 calculated for$[Fe_2(bpmp)(1\text{-}pyace)_2]^{2+}$. The FAB-Mass spectrum of$[ZnFe(bpmp)(1\text{-}pyace)_2](ClO_4)_2$ **ZnFe(1)**, shows peaks at m/z=1268.3 calculated for$[ZnFe(bpmp)(1\text{-}pyace)_2]ClO_4^+$ and m/z=1167.3 calculated for$[ZnFe(bpmp)(1\text{-}pyace)_2]^+$ and m/z=583.7 calculated for$[ZnFe(bpmp)(1\text{-}pyace)_2]^{2+}$. The FAB-Mass spectrum of$[Zn_2(bpmp)(1\text{-}pyace)_2]ClO_4$ **ZnZn(1)** shows a peak at m/z=1179.6 calculated for $[Zn_2(bpmp)(1\text{-}pyace)_2]^+$, and the FAB-Mass spectra for these complexes support that these complexes are synthesized. The absorptions of iron(II) and iron(III) of **FeFe(1)** were observed as 1:1 in the area under the Mössbauer absorption spectrum(δ=0.88 and ΔE=1.24, and δ=0.50 and ΔE=0.48 mm s^{-1} at 293 K) and that of **ZnFe(1)** showed a strong absorption of irons(III) (δ=0.43 and ΔE=0.64 mm s^{-1} at 293 K) with a faint absorption of iron(II).

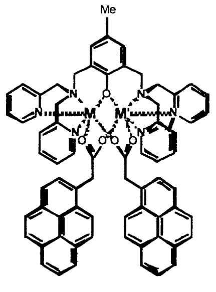

Chart 1. Structure of $[MM'(bpmp)(1\text{-}pyac)_2]^{2+}$.

Emission measurements were carried out in degassed solvent. The fluorescence emission spectra of 1-pyrene acetic acid and its metal complexes were recorded in acetonitrile with the excitation light of 365 nm and are shown in Figure 1. The spectra of the complexes are different from (**1**) in the intensity and the maximum emission wavelength, and are dependent on the nature of the metal ions. The fluorescence emission spectra are composed of monomer-like and excimer emissions. The lowest band of the monomer-like fluorescence pointed at 410 nm is assigned to the lowest energy band (^1L_a) transition of the chromophoric ligand (**1**). The broad excimer emission band with strong intensity is observed at about 490 nm for **ZnZn(1)**. The fluorescences of **ZnFe(1)** and **FeFe(1)** are very weak in intensity compared to that of **ZnZn(1)**, suggesting that the quenching is due to ferric ions. These observations are in good accordance with the results for trichromophoric gallium(III) chelate.[3]

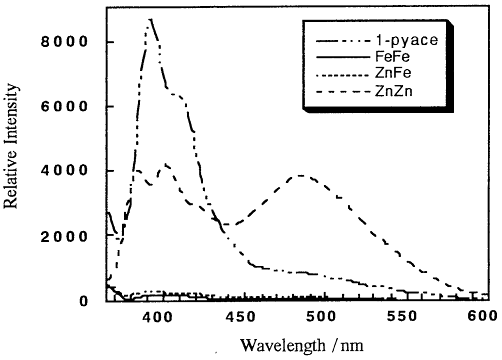

Figure 1. Fluorescence spectra of the complexes and 1-pyreneacetic acid in acetonitrile ($1x10^{-4}$ M).

The concentration dependence of the emission spectra of **ZnZn(1)** is shown in Figure 2. The formation of excimer in the concentration less than 10^{-5} M is believed to result from the intramolecular stacking of the chromophores in solvent. This observation supports that zinc-atom-assisted intersystem crossing does not contribute significantly to the quenching of the chromophore and that the formation of the intramolecular excimer takes place. Increasing the concentration of the complexes brings about an increase in the formation of the excimer at the expense of the monomer-like fluorescence. The maximum emission

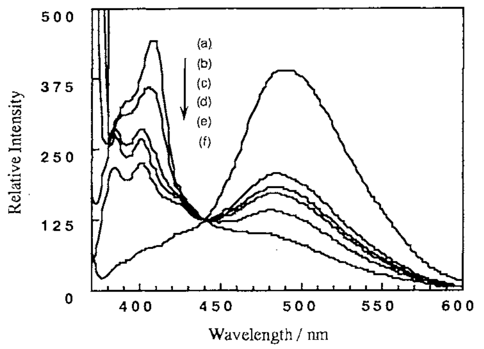

Figure 2. Fluorescence spectra of ZnZn(**1**) in acetonitrile (a) 1x10^{-8}, (b) 1x10^{-7}, (c) 1x10^{-6}, (d) 1x10^{-5}, (e) 1x10^{-4} and (f) 1x10^{-3}M.

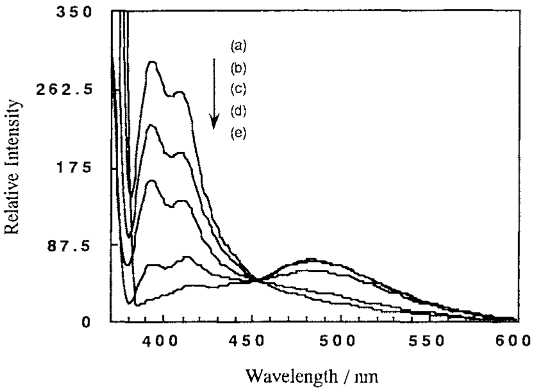

Figure 3. Fluorescence spectra of FeFe(**1**) in acetonitrile (a) 1x10^{-6}, (b) 1x10^{-5}, (c) 1x10^{-4}, (d) 5x10^{-4} and (e) 1x10^{-3}M.

wavelength of the excimer shows red-shift with an increase in the concentration, which suggests that intermolecular excimers are also formed and that the intermolecular excimers are more stable in energy level than the intramolecular excimers. The fluorescence spectra of **FeFe(1)** are shown in Figure 3. If the chromophore is homogeneously dessolved in the solvent, remarkable intermolecular excimer formation would not be expected in the concentration range less than 10^{-4} M. The observations that the excimer formation takes place predominantly in 10^{-4} M and that it is dependent on the concentration of chromophore are explained by thinking that the formation of micelle/aggregation of the complexes begins in 10^{-4} M: the stacking of two chromophores in micelle/aggregation(enhanced local concentration) brings about the intermolecular emission.

The excimer to monomer fluorescence intensity ratios(I_E/I_M) are plotted in Figure 4, and the concentration dependence of **ZnFe(1)** is similar to that of (**1**), suggesting that the chromophore of **ZnFe(1)** behaves as just as chromophore. The

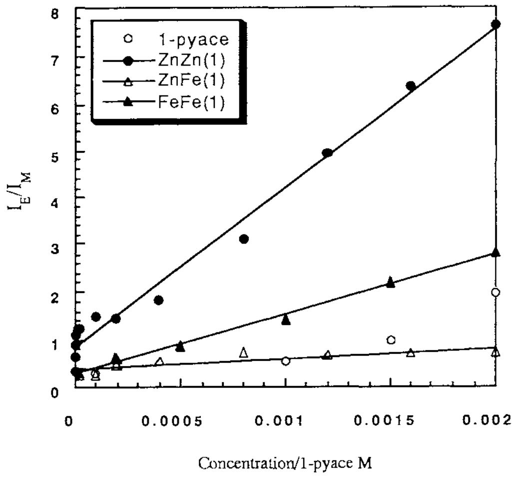

Figure 4. Plots of intensity ratio I_E/I_M vs. the concentration of 1-pyreneacetic acid of the complexes and 1-pyreneacetic acid. Lines are drawn for easy seen.

intensity ratios of **ZnZn(1)** increase more steeply than those of other complexes, suggesting the enhanced intramolecular stacking of the chromophore and/or the formation of the micelle/aggregation. The ratios I_E/I_M are dependent on the excitation wavelength, suggesting that there are ground-state dimers acting as excimer precursors in the solvent, although it is assumed that there are variable conformations in these complexes.[9]

Fluorescence of an nonquenching metal ion Zn(II) is strong in excimer formation, and the concentration-driven phase transition of the complexes and the dissolved state of the complexes in solution would be clear by studying the fluorescence of the complexes.

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