Crystal Structures of 9,10-Bis[bis(2-pyridylmethy)aminomethyl]anthracene and Its $ZnCl_2$ Complex. Intramolecular π–π Interaction between Anthracene and $ZnCl_2$-complexed Pyridine

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Anthracene derivatives having dipicolylaminomethyl group exhibited an emission-intensity enhancement in the presence of Zn^{2+}. On the basis of an X-ray crystallographic analysis, the binding of Zn^{2+} to the dipicolylaminomethyl unit inhibits the photoinduced electron transfer process. Intramolecular π–π interactions between the anthracene and the $ZnCl_2$-complexed pyridine were observed.

Photoresponsive supramolecular systems are of great significance particularly for their potential application to environmental and biological analytical reagent. A number of fluoroionophores have been designed for metal ions,[1] sugers,[2] boronic, and boric acids.[3] Most of them operate by a photoinduced electron transfer (PET) mechanism. The uncomplexed PET fluoroionophore is weak fluorescent, as the photoexcited fluorophore is quenched by the electron transfer from an amine group. Following guest incorporation, the guest-ligand interaction decreases the amine oxidation potential drastically and prevents the electron transfer. As a consequence, the emission intensity of fluorophore is restored. Recently, as a dipicolylamine-based artificial receptor, (9-anthrylmethyl)-bis(2-pyridylmethy)amine (**1**) and 9,10-bis[bis(2-pyridylmethy)-aminomethyl]anthracene (**2**) have been reported by Bhattacharya,[4] de Silva,[5] and Hamachi group.[6] However the complexation behavior of **1** and **2** with $ZnCl_2$ was not investigated in detail. In order to elucidate the metal cation induced fluorescence enhancement, we now report the complexation behavior of **1** and **2**.

UV spectral behaviour of **1** and **2** with $ZnCl_2$ was shown in Figures 1 and 2. The spectra of **1** and **2** were similar to those of 9-methylanthracene (9-MA) and 9,10-dimethylanthracene (9,10-DMA). On addition of guest salts, the UV absorption spectra of **1** and **2** changed in CH_3OH. On addition of $ZnCl_2$ to **1** and **2** disappeared the original absorption bands (assigned to anthracene unit) of **1** and **2** and new absorption bands at longer wavelength by 5.4 nm for **1** and 8.5 nm for **2**, respectively, appeared. It is, thus, expected that there is an appreciable interaction between the $ZnCl_2$-complexed pyridine and anthracene rings.

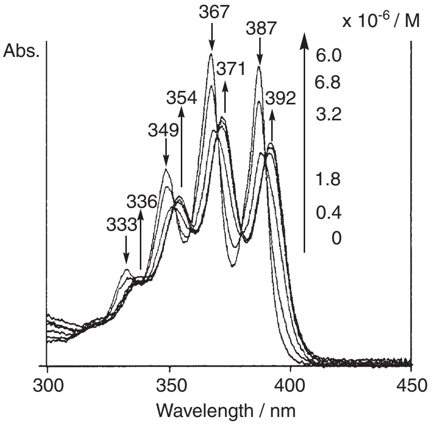

Figure 1. Absorption spectra of **1** (4.0×10^{-6} M) in the presence of $ZnCl_2$ (0–6.0×10^{-6} M) in CH_3OH.

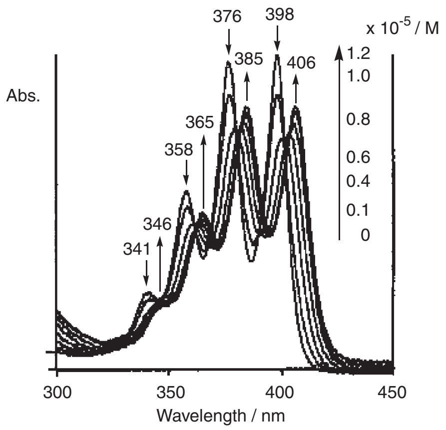

Figure 2. Absorption spectra of **2** (4.0×10^{-6} M) in the presence of $ZnCl_2$ (0–1.2×10^{-5} M) in CH_3OH.

Fluorescence spectral behavior of **1** and **2** (4.0×10^{-6} M) gave weak emission bands. The emission-band intensities of **1** and **2** were reduced to approximately 1/12 and 1/412 that of the corresponding standard substance (9-MA for **1**, 9,10-DMA for **2**: 4.0×10^{-6} M). This indicates that the quenching of the excited-state anthracene chromophore by the dipicolylamine unit proceeds in a mechanism similar to that for the classical fluorescent-aliphatic amine system.[7] Instead of emission quantum yield, a measure of the guest cation-induced fluorescence recovery would express as a emission intensity ratio ($I_{\mathrm{complex}}/I_{\mathrm{standard}}$) of guest cation complexes to the corresponding standard substance (9-MA, 9,10-DMA). The $I_2/I_{9,10\text{-DMA}}$ value (2.4×10^{-3}) of **2** to 9,10-DMA is lower than that ($I_1/I_{9\text{-MA}}$: 8.1×10^{-2}) of **1** to 9-MA. This means the PET from the nitrogen atoms in the two dipicolylamines to excited fluorescent moieties occurrs efficiently.

In Figure 3 is illustrated the fluorescence spectral behavior of **1** and **2** (4.00×10^{-6} M) in the presence of $ZnCl_2$ at room tempereture. Emission enhancements of **1** and **2** were observed upon the addition of various amounts of $ZnCl_2$. The **1**$\cdot ZnCl_2$ and **2**$\cdot 2ZnCl_2$ complexes had strong emission bands ($I_{1\cdot \mathrm{Zn}}/I_1 = 17$, $I_{2\cdot \mathrm{Zn}}/I_2 = 330$) at larger wavelength than those

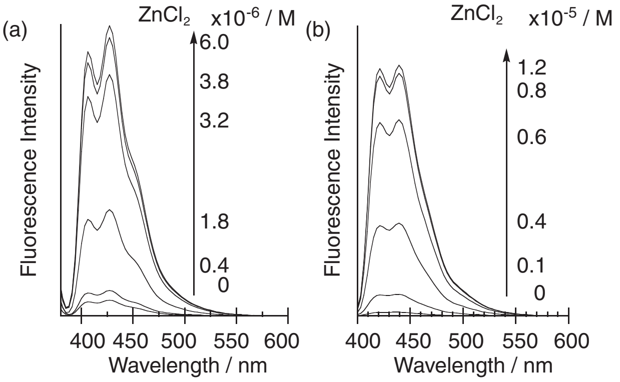

Figure 3. Emission Spectra of (a) **1** and (b) **2** (4.0×10^{-6} M) in the presence of $ZnCl_2$ in CH_3OH. Excited at 371 nm for **1** and 385 nm for **2**.

of free host. The $I_{\mathrm{complex}}/I_{\mathrm{standard}}$ values were 1.4 for **1**·$ZnCl_2$ and 0.80 for **2**·2$ZnCl_2$, respectively. Suprisingly, the emission intensity of **1**·$ZnCl_2$ is larger than that of 9-methylanthracene. This suggests that the complexation produces not only prevention of PET process but also an interaction between the anthracene and the $ZnCl_2$-complexed pyridine.

The molecular structures[8] of **2** and its zinc dichloride complex were elucidated by X-ray crystallographic anlysis as shown in Figure 4.

The compound (**2**) forms a 1:2 complex with $ZnCl_2$. The two Zn^{2+} cations have a tetrahedral coordination involving the two pyridine N atoms of picolylamine units and two Cl atoms of chloride anions. The coordinated structure of **2**·2$ZnCl_2$ is similar to that of dichlorobis(pyridine)zinc(II) complex.[9] Interestingly, two intramolecular π–π interactions between the pyridine and anthracene rings of **2**·2$ZnCl_2$ were observed. The distance between the intramolecular pyridine planes is 3.20 Å for C6· · ·C10, which is within the range[10] of the π–π interaction. This means that intramolecular charge transfer can take place readily between anthracene and $ZnCl_2$-complexed pyridine ring in the ground state.

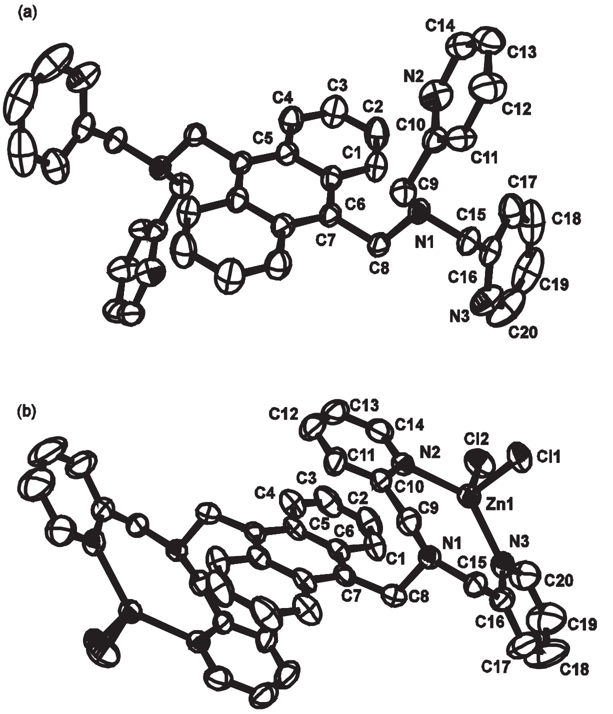

Figure 4. Molecular structures of (a) **2** and (b) **2**·2$ZnCl_2$.

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8 Single crystals suitable for crystallography were obtained from a solution of **2** and **2**·2$ZnCl_2$ in methanol. All three structures were solved by direct method (SIR92).[11] The teXsan for windows version 1.06[12] and SHELX-97[13] packages were used for other calculations. Crystal data for **2**: $C_{40}H_{36}N_6$, $M_r = 600.75$, monoclinic, $P2_1/n$, $a = 10.6490(10)$, $b = 10.7054(8)$, $c = 15.1380(14)$ Å, $\beta = 102.479\ (3)^\circ$, $V = 1685.0(3)$ Å^3, $Z = 2$, $T = 213$ K, $d_{\mathrm{calcd}} = 1.184\ \mathrm{g\,cm^{-3}}$, $F(000) = 636.00$, $\mu(\mathrm{Mo\ K}\alpha) = 0.071\ \mathrm{cm^{-1}}$, $\lambda(\mathrm{Mo\ K}\alpha) = 0.71069$ Å, 3827 reflections measured, 3058 observed, 209 variables, $R[F^2 > 2\sigma(F^2)] = 0.0735$, $wR(F^2) = 0.2673$. Crystal data for **2**·2$ZnCl_2$: $C_{40}H_{36}N_6Zn_2Cl_4$, $M_r = 873.34$, monoclinic, $P2_1/n$, $a = 10.3207(7)$, $b = 14.8998(10)$, $c = 12.8756(9)$ Å, $\beta = 101.4580(10)^\circ$, $V = 1940.5(2)$ Å^3, $Z = 2$, $T = 296$ K, $d_{\mathrm{calcd}} = 1.495\ \mathrm{g\,cm^{-3}}$, $F(000) = 892.00$, $\mu(\mathrm{Mo\ K}\alpha) = 15.49\ \mathrm{cm^{-1}}$, $\lambda(\mathrm{Mo\ K}\alpha) = 0.71069$ Å, 8401 reflections measured, 4462 observed, 235 variables, $R[F^2 > 2\sigma(F^2)] = 0.0500$, $wR(F^2) = 0.1797$.

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