

A Functionalized Fluorescent 7-(4-Methoxybenzoylamino)dipyrido[3,2-a:2',3'-c]phenazine (7-(4-mba)dppz) Having Metal Ion Sensing Ability

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Fluorescent materials are attracting considerable interest for their potential sensory, biomedical, medical, and photo-electronic applications.^{1,2} In particular, fluorescent materials with the 2,2'-bipyridine (bpy) unit have been studied because of their excellent properties as bidentate ligands and as hydrogen bond acceptors.³ Furthermore, we reported that 7-(4-methoxybenzoylamino)dipyrido[3,2-a:2',3'-c]phenazine (7-(4-mba)dppz) has a relatively high fluorescence quantum yield ($\Phi = 0.24$) comparable to that of the 7-aminodipyrido[3,2-a:2',3'-c]phenazine (7-amino-dppz) ($\Phi = 0.21$), despite being a nonrigid π -conjugated system.⁴ The photophysical properties of 7-(4-mba)dppz (**1**) as a ligand in the presence of different metal cations (Mg^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+}) were investigated in acetonitrile solution in view of potential application as the metal ion sensor. Acetonitrile has been chosen as a good solvent for all the spectral measurements in the presence of metal cations. Here we report the absorption and emission spectroscopic behavior which include the results of complexation ratio related to $[\text{metal ion}]/[\mathbf{1}]$. All spectroscopic measurements were carried out with $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) in acetonitrile at room temperature. Thus, every titration experiment was carried out by adding metal ion in 0.1 equivalent increments to $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ of 7-(4-mba)dppz (**1**) in acetonitrile at room temperature.

As shown in Figure 1, the change in absorption bands was observed when Mg^{2+} ion in acetonitrile was added to $6.00 \times$

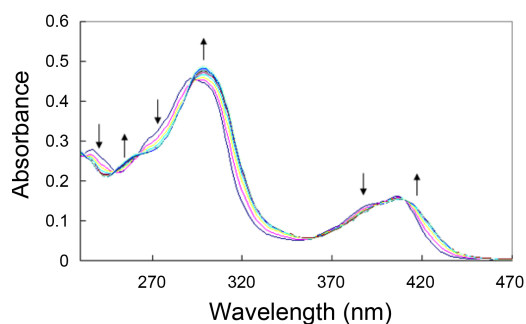


Figure 1. The change of electronic absorption spectra of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) by addition of Mg^{2+} ion in acetonitrile at room temperature.

$10^{-6} \text{ mol dm}^{-3}$ of 7-(4-mba)dppz (**1**) in acetonitrile at room temperature. The absorption peaks of 7-(4-mba)dppz (**1**) were found at 295 nm and 410 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively, along with the absorption shoulders at 270 nm and 385 nm. The isosbestic points were observed at 250 nm, 260 nm, 295 nm, 365 nm, 395 nm. The two absorption peaks of 7-(4-mba)dppz (**1**) were red-shifted to 300 nm and 415 nm, respectively, upon addition of Mg^{2+} cations in the presence of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)-dppz (**1**) in acetonitrile.

The hyperchromic effect on the absorption peak of 300 nm was also observed. This hyperchromic effect appeared remarkably in the case of the addition of Ni^{2+} ion and Cu^{2+} ion, respectively, as shown in Figure 2. The two absorption peaks of 7-(4-mba)dppz (**1**) were remarkably red-shifted to 300 nm and 415 nm, respectively, upon addition of metal ion (Ni^{2+} or Cu^{2+}) in the presence of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) in acetonitrile.

For Zn^{2+} ion, the change of absorption pattern was almost the same as in the case of Mg^{2+} ion. These results indicate that the electron-donating phenanthroline moiety of 7-(4-mba)dppz (**1**) in the ground state participates in bidentate complexation.

Meanwhile, as shown in Figure 3, when 7-(4-mba)dppz (**1**) was excited at 365 nm, the fluorescence emission peak appeared at 454 nm. This fluorescence emission peak was red-shifted to 475 nm having the isoemissive point at 460

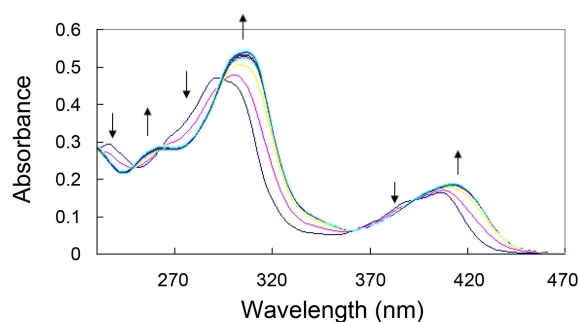


Figure 2. The change of electronic absorption spectra of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) by addition of metal ion (Ni^{2+} or Cu^{2+}) in acetonitrile at room temperature.

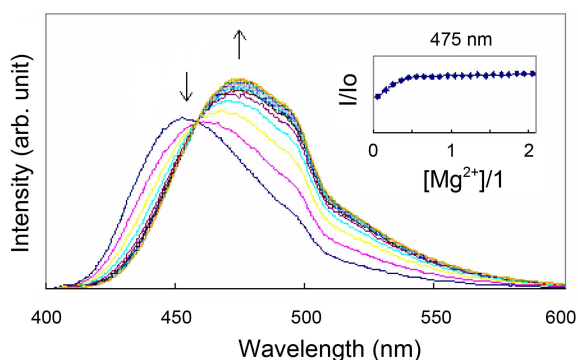


Figure 3. The fluorescence spectral titration of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) by addition of Mg^{2+} ion in acetonitrile at room temperature.

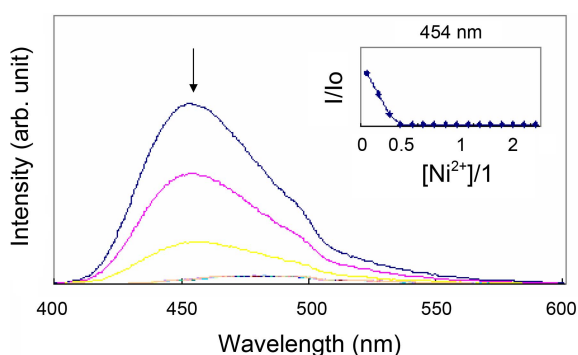


Figure 4. The fluorescence spectral titration of $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) by addition of Ni^{2+} ion in acetonitrile at room temperature.

nm, when Mg^{2+} ion in acetonitrile was added to $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ of 7-(4-mba)dppz (**1**) in acetonitrile at room temperature. Thus, this fluorescence emission peak of 475 nm was shown the increasing pattern. This behavior also appeared in the case of the addition of Zn^{2+} ion and the fluorescence emission peak was red-shifted to 480 nm. However, as shown in Figure 4, for Ni^{2+} ion, it is seen that the fluorescence emission intensity decreases although a little red-shift was shown. This behavior also appeared in the case of addition of Cu^{2+} ion. From these results, we were known that the fluorescence emission intensities of 7-(4-mba)dppz (**1**) increase in the presence of Mg^{2+} and Zn^{2+} , respectively, in contrast to decreasing in the presence of Ni^{2+} and Cu^{2+} , respectively. As shown in the inset (Fig. 3), when the change of the fluorescence emission intensity was plotted as the complexation ratio related to $[\text{Mg}^{2+} \text{ ion}]/[\mathbf{1}]$ at the emission wavelength 475 nm, it was shown the complex structure of $[\text{Mg}^{2+} \text{ ion}]:[\mathbf{1}] = 1:2$. Also, when it was plotted as the complexation ratio related to $[\text{Zn}^{2+} \text{ ion}]/[\mathbf{1}]$ at the emission wavelength 480 nm, the result was the same as the ratio $[\text{Mg}^{2+} \text{ ion}]:[\mathbf{1}] = 1:2$. Furthermore, as shown in the inset (Fig. 4), when it was plotted as the complexation ratio related to $[\text{Ni}^{2+} \text{ ion}]/[\mathbf{1}]$ at the emission wavelength 454 nm, the result was shown as the ratio $[\text{Ni}^{2+} \text{ ion}]:[\mathbf{1}] = 1:2$. For Cu^{2+} ion, the result was the same as the ratio $[\text{Ni}^{2+} \text{ ion}]:[\mathbf{1}] = 1:2$. Interestingly, we found that all the complexation ratio were the same as $[\text{M}^{2+} \text{ ion}]:[\mathbf{1}] = 1:2$, as shown in Figure 5.

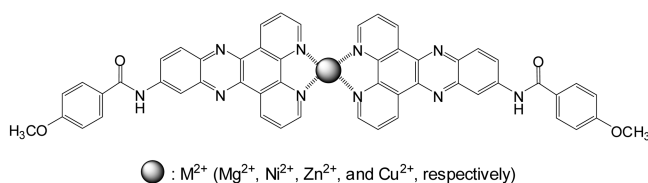


Figure 5. The complex structure of $[\text{M}^{2+}]:[\mathbf{1}] = 1:2$ appeared in $6.00 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) in acetonitrile at room temperature.

In conclusion we suggest that 7-(4-mba)dppz (**1**) can have a potential application for the cation sensor material such as divalent Ni^{2+} and Cu^{2+} metal ions.

Experimental Section

Materials. Spectroscopic grade of acetonitrile (Aldrich) was used for the spectroscopic measurement. 7-(4-mba)dppz (**1**) was synthesized according to a previously reported procedure.⁴ The following Aldrich grade salts were used for the spectroscopic measurement; MgClO_4 , NiClO_4 , CuClO_4 , ZnClO_4 .

Measurements. The absorption spectra were measured on a Hitachi U-3300 spectrophotometer. The fluorescence spectra were measured on a SLM8100 spectrofluorometer (Aminco, USA) with a Xe-arc lamp light source using 4 or 8 nm band pass excitation and emission monochromators, in which the rhodamine B solution was used as a reference to correct for variation of the Xe light source with time and wavelength. All spectroscopic measurements were carried out in the presence of $6 \times 10^{-6} \text{ mol dm}^{-3}$ 7-(4-mba)dppz (**1**) in acetonitrile.

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