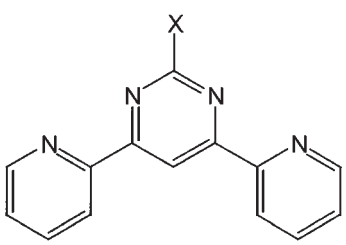
Syntheses of New Pyrimidine Based Compounds and Their Peculiar Emission Behaviors

Shigeru Takagi,* Tomohiro Sahashi, Katsuya Sako,† Katsuya Mizuno,†† Masato Kurihara,†† and Hiroshi Nishihara††
Department of Environmental Technology and Urban Planning, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555
†*Department of Systems Management of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555*
††*Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033*

(Received March 4, 2002; CL-020196)

A series of pyrimidine-based compounds have been synthesized. Methyl (**1**) and amino (**2**) substituted compounds emitted fluorescence in solution. From the solvent effect on their emission spectra, the mechanism of emission was different in **1** and **2**, and the emission of **2** contains the internal charge transfer process.

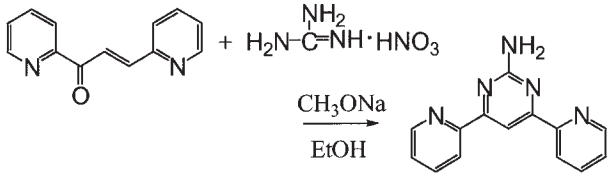
Pyrimidine based multidentate ligands have been actively used for multi metal systems such as supra-molecular metal complexes. Although many kinds of pyrimidine based oligopyridine ligands have been reported by now, it seems that the variation is not yet enough for the development of supramolecular chemistry. For construction of more complicated ligands, it is very useful to introduce the various functional groups at the 2-position of the pyrimidine. We chose the compound shown in Figure 1 as a building block, and introduced various functional groups into the position of X. Here, we report the syntheses of several kinds of pyrimidine based compounds ($X = NH_2$, Cl, CH_2Br, $CHBr_2$, CBr_3), and also describe their peculiar emission properties.



1 X = CH_3
2 X = NH_2
3 X = Cl
4 X = CH_2Br
5 X = $CHBr_2$
6 X = CBr_3

Figure 1. Compounds **1**–**6**.

For the preparation of pyrimidine derivatives, the condensation of β-diketone with amidine is a common method. For instance, known compounds, **1** and X = H, were easily synthesized by use of this strategy.[1] We thought that the amino group was considerably promising as a starting material for facile introduction of various functional groups, and we have tried to synthesize **2**. Jones and Glass have reported that **2** could not be synthesized by use of condensation of dione with guanidine or amidine.[2] After various conditions were examined, we finally synthesized **2** in 40% yield by condensation of guanidine nitrate with 1,3-di-(2′-pyridyl)-2-propen-1-one.[3] Compound **3**[4] was synthesized from **2** by use of Sandmeyer reaction in satisfactory yield (52%).[5] The halogen substitution of the methyl group was a useful means for further modification of position X. Therefore, we have carried out the bromination of the methyl group. The monosubstituted **4**[6] was synthesized in 11% yield by use of NBS,[7] and tri-substituted **6**[8] was synthesized by use of bromine.[9] The disubstituted **5**[10] was obtained by reducing **6** with tin metal.[11] Small amount of impurities were included in **5** and **6**, and satisfying data were not obtained in their elemental analyses.



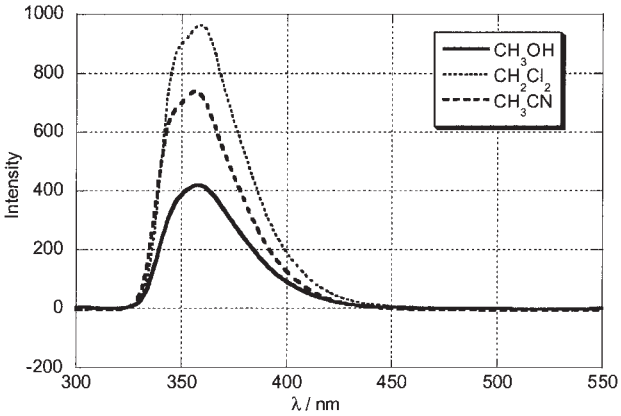


Figure 2. Solvent effect on emission spectra of **1**.

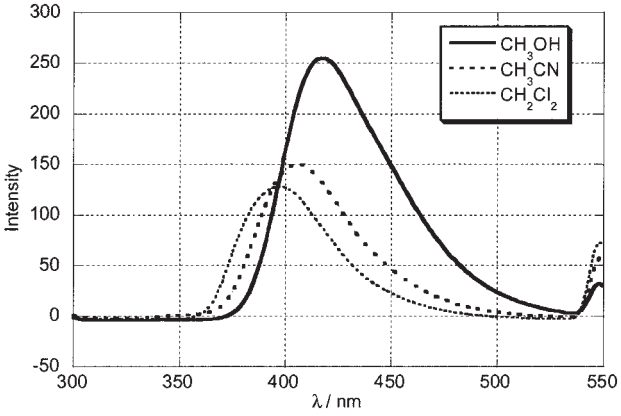


Figure 3. Solvent effect on emission spectra of **2**.

Compound **1** and **2** emitted fluorescence in solution.[12] Other compounds did not emit fluorescence at all. When the solvent effect on the emission spectra was examined, quite different results were obtained in **1** and **2**. In **1**, the emission intensity

decrease in order of $CH_2Cl_2 > CH_3CN > CH_3OH$, and the emission maximum is slightly blue shifted in the same order. Judging from its spectrum shape, the spectrum is composed of two emission bands, the dominant long-wave emission band (band I) and the small short-wave emission band (band II). Both intensity and maximum position of band II vary with the solvent, though those of band I are hardly changed. On the other hand, an almost opposite tendency is observed in the emission spectra of **2**. The emission intensity increased in order of $CH_2Cl_2 < CH_3CN < CH_3OH$, and the emission maximum red-shifted in the same order. As for **2**, the emission is composed of two emission bands. The higher energy band is decreased while changing the solvent from CH_2Cl_2 to CH_3OH, and the lower energy band increased and red-shifted. For the absorption spectra, solvent effect was hardly observed in **1**; however, the absorption band of **2** at about 350 nm red-shifted by 5 nm when the solvent was changed from CH_2Cl_2 to CH_3OH. These data indicate that the mechanism of emission is different in **1** and **2**. Electron donor-acceptor molecules linked by a single bond have been used for studying the intramolecular charge transfer complexes. The emission of the 4-(dimethylamino)-pyrimidine[13] and 4-(dimethylamino)-pyridine[14] in polar solvents consists of a normal emission and an anomalous emission. The maximum of the normal emission band is around 350 nm, and the position of the anomalous emission depends on the particular solvent used and its maximum is in the region between 420 and 520 nm. This anomalous fluorescence results from internal charge-transfer state. The anomalous emission is only observed in sufficiently polar solvents. The intensity of normal emission decreases with an increase in the solvent polarity. The solvent effects on the emission of **1** and **2** can be roughly explained by the following ideas; the dominant emission band in **1** and the short-wave emission in **2** originate in their initially excited singlet states and the long-wave emission in **2** originates in its charge-transfer state. In 4-aminopyrimidine, only a very weak primary excited emission is observed. This lack of CT emission is caused by rather higher oxidation potential of the amino derivative compared with the dialkylamino derivative.[13] To clarify the reason why CT emission is observed in **2**, quantum chemical calculation of the HOMO/LUMO gaps of **2**, 2-aminopyrimidine, 4-aminopyrimidine, and 4-(dimethylamino)-pyrimidine.[15] As a result, the values of the gaps became in the following order; 2-aminopyrimidine > 4-aminopyrimidine > 4-(dimethylamino)-pyrimidine > **2**. This result indicates that the oxidation of amino group of **2** is fairly easy. Therefore, the CT emission was observed in **2**.

References and Notes

1 a) G. S. Hanan, U. S. Schubert, D. Volkmer, E. Rivié, J.-M. Lehn, N. Kyritsakas, and J. Fischer, *Can. J. Chem.*, **75**, 169 (1997). b) G. S. Hanan, C. R. Arana, J.-M. Lehn, and D. Fenske, *Angew. Chem. Int. Ed. Engl.*, **34**, 1122 (1995).

2 P. D. Jones and T. E. Glass, *Tetrahedron Lett.*, **42**, 2265 (2001).

3 Anal. Found: C, 67.49; H, 4.48; N, 28.11%. Calcd for $C_{14}H_{11}N_5$: C, 67.46; H, 4.45; N, 28.10%. ^{1}H-NMR ($CDCl_3$, δ): 5.23 (2H, s, NH_2), 7.40, 7.84, 8.36, 8.73 (8H, m, pyridine), 8.63 (1H, s, pyrimidine). MS-FAB m/z 250.2 $[M + H]^+$.

4 Anal Found: C, 62.63; H, 3.37; N, 20.87%. Calcd for $C_{14}H_9N_4Cl$: C, 62.58; H, 3.38; N, 20.85%. ^{1}H-NMR ($CDCl_3$, δ): 7.45, 7.88, 8.51, 8.78 (8H, m, pyridine), 9.36 (1H, s, pyrimidine). MS-FAB *m/z*(%) 269.1 (100), 271.1 (33) $[M + H]^+$.

5 Org. Syn. Collective Volume, 4, 182.

6 Anal. Found: C, 55.23; H, 3.40; N, 17.16%. Calcd for $C_{15}H_{11}N_4Br$: C, 55.06; H, 3.39; N, 17.12%. ^{1}H-NMR ($CDCl_3$, δ): 4.77 (2H, s, CH_2Br) 7.44, 7.88, 8.56, 8.78 (8H, m, pyridine), 9.21 (1H, s, pyrimidine). MS-FAB m/z(%) 327.1 (100), 329.1 (100) $[M + H]^+$.

7 M. M. El-Kerdawy, A. A. El-Eman, and H. I. El-Subbagh, *J. Heterocyclic Chem.*, **26**, 913 (1989).

8 ^{1}H-NMR ($CDCl_3$, δ): 7.47, 7.91, 8.68, 8.80 (8H, m, pyridine), 9.35 (1H, s, pyrimidine). MS-FAB m/z(%) 482.9 (33), 484.9 (100), 486.9 (100), 488.9 (33) $[M + H]^+$.

9 W. K. Hagmann, F. Z. Basha, M. Hashimoto, R. B. Frye, S. Kojo, and S. M. Hecht, *J. Org. Chem.*, **46**, 1413 (1981).

10 ^{1}H-NMR ($CDCl_3$, δ): 6.88 (1H, s, $CHBr_2$) 7.46, 7.91, 8.61, 8.80 (8H, m, pyridine), 9.33 (1H, s, pyrimidine). MS-FAB m/z(%) 405.0 (51), 407.0 (100), 409.0 (50) $[M + H]^+$.

11 M. P. L. Caton, M. S. Grant, D. L. Pain, and R. Slack, *J. Chem. Soc.*, **4**, 5467 (1965).

12 Quantum yields (QY) were calculated using as a reference *p*-terphenyl in cyclohexane. (QY = 0.87) **1**; QY = 0.042 (CH_3OH, excited at 283 nm), **2**; QY = 0.011 (CH_3OH, excited at 274 nm).

13 a) J. Herbich, Z. R. Grabowski, H. Wójtowicz, and K. Golankiewicz, *J. Phys. Chem.*, **93**, 3439 (1989). b) W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. K. Kühnle, and K. A. Zachariasse, *J. Phys. Chem.*, **96**, 10809 (1992).

14 J. Herbich and J. Waluk, *Chem. Phys.*, **188**, 247 (1994).

15 Calculations were performed by use of Quantum Cache 4.0.